

# 1. The Orbital Picture of Electronic Structure

Spectroscopy—since it is perhaps the only “direct experimental measurement” of quantum effects used by chemists—is one of the most important motivations for computational methods. When interpreting spectra, it is important to have computational methods for assigning each observed transition to a specific molecular state and to have an “orbital-based” picture of that molecular state. However, computational methods extend beyond the realm of spectroscopy to kinetics, thermodynamics, and many other molecular properties. Computational techniques, then, are important “supporting tools” for a wide variety of experiments and, just as important, they are very useful when experiments cannot be performed (as for modeling the chemistry in interstellar space or the upper atmosphere), are dangerous or expensive to perform (as the chemistry in a nuclear waste dump or at deep-sea vents), or raise ethical issues (as in the testing of biologically active compounds in pharmaceuticals or cosmetics). Indeed, computational chemistry techniques have been used in each of the above contexts, with high-profile results related to the debate over life on Mars, the role of surface chemistry in ozone depletion, the role of aerosols in acid rain....

It is important, then, that we understand the “big ideas” behind computational methods, then, at least to the point that we can use them intelligently to obtain reliable results and predictions.

## I. Review

### A. The Orbital Model

In chemistry, we often think about electrons occupying orbitals. This is an approximate picture: it is only rigorously correct for one-electron systems. In one-electron atoms, the electron occupies the 1s, or 2s, or 2p, or . . . orbital. Similarly, in a one-electron molecules the electron occupies a molecular orbital. Moreover, each molecular orbital can be written as a linear combination of atomic orbitals,

$$\psi_{MO}(\mathbf{r}) = \sum_{A=1}^{N_{\text{atoms}}} \sum_{i=1}^{\infty} c_{iA} \phi_{iA}(\mathbf{r}) \quad (1.1)$$

where  $\psi_{MO}(\mathbf{r})$  is a molecular orbital and  $\phi_{iA}(\mathbf{r})$  is the  $i^{\text{th}}$  orbital on atom  $A$ . When all the atoms in a one-electron molecule are very far apart, only one (for molecules where no two atoms are the same) or a few (there can be up to  $m$  non-zero  $c$ 's for molecules with  $m$  atoms of the same type) of the coefficients (denoted  $c_{iA}$ ) will not be zero. For molecules near equilibrium, no coefficient is zero unless it is constrained to be zero by symmetry (or, very occasionally, accidental degeneracy). As long as the sum over the atoms,  $A$ , includes every atom in the molecule and the sum over orbitals,  $i$ , includes every orbital, denoted  $\phi_{iA}(\mathbf{r})$ , of each atom, then Eq. (1.1) is exact. Of course, in practice the sum over atomic orbitals is restricted to “reasonable” orbitals, so that ground-state molecular orbital in  $\text{H}_2^+$  might be represented as<sup>1</sup>

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<sup>1</sup> Why did I put a minus sign in front of the  $p$ -orbitals in Eqs. (1.2) and (1.3), but not the  $s$  or the  $d$  orbitals? If you were to write the next term in this expansion (including  $f$  orbitals), would the coefficient of the  $f$  orbital be positive or negative?

$$\begin{aligned}\psi_{\sigma_1}(\mathbf{r}) \approx & c_{1,1s}\phi_{1,1s}(\mathbf{r}) + c_{1,2s}\phi_{1,2s}(\mathbf{r}) - c_{1,2p_z}\phi_{1,2p_z}(\mathbf{r}) \\ & + c_{2,1s}\phi_{2,1s}(\mathbf{r}) + c_{1,2s}\phi_{1,2s}(\mathbf{r}) - c_{1,2p_z}\phi_{1,2p_z}(\mathbf{r})\end{aligned}\quad (1.2)$$

Equation (1.2) is approximate and would be improved, for example, by adding some additional terms<sup>2</sup>

$$\begin{aligned}\psi_{\sigma_1}(\mathbf{r}) \approx & c_{1,1s}\phi_{1,1s}(\mathbf{r}) + c_{1,2s}\phi_{1,2s}(\mathbf{r}) - c_{1,2p_z}\phi_{1,2p_z}(\mathbf{r}) + c_{1,3s}\psi_{3s}(\mathbf{r}) - c_{1,3p_z}\psi_{3p_z}(\mathbf{r}) + c_{1,3d_{z^2}}\psi_{3d_{z^2}}(\mathbf{r}) \\ & + c_{2,1s}\phi_{2,1s}(\mathbf{r}) + c_{1,2s}\phi_{1,2s}(\mathbf{r}) - c_{1,2p_z}\phi_{1,2p_z}(\mathbf{r}) + c_{2,3s}\psi_{3s}(\mathbf{r}) - c_{2,3p_z}\psi_{3p_z}(\mathbf{r}) + c_{2,3d_{z^2}}\psi_{3d_{z^2}}(\mathbf{r})\end{aligned}\quad (1.3)$$

Knowing how many atomic orbitals we must consider in order to accurately describe a molecular orbital is one of the things we shall discuss in our course.

Just because the picture of electrons as occupying orbitals is only exact for one-electron systems does not mean it is not useful for systems with more electrons. Indeed, way back in general chemistry we learned that we could describe, say, the Neon atom as having the “electron configuration”  $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2$ , with one “spin up” electron in the  $1s$  orbital and one “spin down” electron in the  $1s$  orbital. Similarly, there are two electrons in the  $2s$  orbital (one with spin up and one with spin down). And so on. In each case, the Pauli exclusion principle tells us that we can never have two electrons in the same state, so if we put two electrons in the same orbital, then they must have different spin.<sup>3</sup>

Why can we think about electrons as occupying “atomic orbitals?” Even though it is not “exact” to describe the Neon atom with the electron configuration  $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2$ , this is a reasonable approximation.<sup>4</sup> The core idea is that we can think about the electrons in the Neon atom as feeling a repulsion from the “average” of the other electrons in the system. For example, a  $2s$  electron in Neon will feel an attractive potential from the nucleus, a repulsive potential from the two  $1s$  electrons, a repulsive potential from the other  $2s$  electron, and a repulsive potential from the six  $2p$  electrons. Recalling that the probability of observing an electron in orbital  $i$  at the point  $\mathbf{r}$  is just  $|\phi_i(\mathbf{r})|^2$ , we would consider that an electron in a  $2s$  orbital would feel an “average repulsive potential” due to the other electrons given by

<sup>2</sup> Equations (1.2) and (1.3) are example of a case where some of the coefficients of the molecular orbitals are zero by symmetry. In this case, the fact that there is no orbital angular momentum around the bond axis (conventionally assumed to be the  $z$ -axis) in a  $\sigma$ -orbital means that the coefficients of the  $p$ ,  $d$ ,  $f$ , ... orbitals with nonzero angular momentum about the  $z$ -axis are all zero.

<sup>3</sup> Based on the fact that no two electrons can ever have the same state, can you explain why we can never put more than two electrons in the same orbital? Suppose that, in some alternative universe, there were three choices for direction of the electron’s spin, “up,” “down,” and “sideways.” What would be the electron configuration of Neon in this universe? How many electrons would there be in the first two “inert gasses?”

<sup>4</sup> The idea of an electron configuration is not exact for systems with more than one electron even when there are not very many electrons. For example, the Helium atom can be described as having a  $1s^2$  electron configuration. However, even describing the *ground state* of the Helium atom requires that we consider also the  $2p^2$ ,  $2s^2$ ,  $3s^2$ ,  $3d^2$ , ... configurations also. (One can think of this as reflecting the fact that when two electrons are crammed into the same orbital, they “bump into each other” and cause each other to “swerve.” Describing this “swerving” requires that one consider “excited states.” For example, considering the  $2p^2$  excited state helps explain the fact that if one electron is on one side of the nucleus, the other one tends to “swerve” over to the other side of the nucleus. Similarly, the  $2s^2$  configuration helps explain the fact that if one electron is close to the nucleus, the other tends to swerve away from the nucleus. Why might you expect that  $1s^2 2s^2 2p_x^2 2p_y^2 3p_z^2$ ,  $1s^2 2s^2 2p_x^2 3p_y^2 2p_z^2$ ,  $1s^2 2s^2 3p_x^2 2p_y^2 2p_z^2$ , and  $1s^2 3s^2 2p_x^2 2p_y^2 2p_z^2$  electron configurations would be important for describing the ground state of Neon? What sorts of “correlations” between the motion of the electrons do each of these configurations describe?

$$\begin{aligned}\Phi_{2s}(r) = \Phi_{2s}(\mathbf{r}) = & \int \frac{2|\phi_{1s}(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + \int \frac{|\phi_{2s}(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' \\ & + \int \frac{2|\phi_{2p_x}(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + \int \frac{2|\phi_{2p_y}(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + \int \frac{2|\phi_{2p_z}(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}'\end{aligned}\quad (1.4)$$

In this case, the “average” repulsive potential felt by the electron is spherically symmetric, so  $\Phi_{2s}(\mathbf{r}) = \Phi_{2s}(r)$ .<sup>5</sup>

Now, the electron in the  $2s$  orbital feels an attractive potential towards the nucleus and a repulsive potential from the “average” of the other electrons. Specifically,

$$V_{2s}^{(avg)}(r) = -\frac{Z}{r} + \Phi_{2s}(r), \quad (1.5)$$

where  $Z = 10$  is the atomic number of Neon. We often, then, rewrite the repulsive potential due to the other electrons as a “screening function,”

$$s_{2s}(r) = r\Phi_{2s}(r) \quad (1.6)$$

so that

$$\begin{aligned}V_{2s}^{(avg)}(r) &= -\frac{Z + s_{2s}(r)}{r} \\ &= -\frac{Z_{eff,2s}(r)}{r}\end{aligned}\quad (1.7)$$

Equation (1.7) defines the effective nuclear charge felt by an electron.

Since an electron in a  $2s$  orbital feels a “average” potential given by Eq. (1.7), we can write the Hamiltonian for this orbital as

$$\left(-\frac{\nabla^2}{2} - \frac{Z_{eff,2s}(r)}{r}\right)\phi_{2s}(r) = \varepsilon_{2s}\phi_{2s}(r) \quad (1.8)$$

Here  $\varepsilon_{2s}$  is the “orbital energy” of the electron in the  $2s$  orbital. The interpretation of the  $2s$  orbital in Neon, then, is that it is solution to a one-electron Schrödinger equation where the potential is not only the potential of the bare nucleus, but also includes the “average” potential a  $2s$  electron feels due to the “cloud” of other electrons in the system. (Detailed interactions between the electrons are neglected.)

Based on this insight, we can write a more general equation, valid for the molecular orbitals in any system

$$\left(-\frac{\nabla^2}{2} + v(\mathbf{r}) + \hat{w}(\mathbf{r})\right)\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r}). \quad (1.9)$$

The concept, again, is that molecular orbitals arise as solutions to a one-electron Hamiltonian. Here,  $v(\mathbf{r})$  is called the external potential; it accounts for all the electrostatic forces on the system that are not due to other electrons and, for an isolated molecule, simply reproduces the electron-nuclear attraction energy,

$$v(\mathbf{r}) = -\sum_{\alpha=1}^P \frac{Z_{\alpha}}{|\mathbf{r}-\mathbf{R}_{\alpha}|}. \quad (1.10)$$

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<sup>5</sup> This would not necessarily be true for a  $2p$  electron. Can you explain why  $\Phi_{2p_x}(\mathbf{r})$  would not be spherically symmetric, even though  $\Phi_{2s}(\mathbf{r})$  and  $\Phi_{1s}(\mathbf{r})$  are?

The quantity  $\hat{w}(\mathbf{r})$  may be termed the “internal potential.” The internal potential represents the average potential an electron in orbital  $\psi_i(\mathbf{r})$  at  $\mathbf{r}$  feels due to the “cloud” of other electrons. Models for electronic structure that are based on Eq. (1.9) are often called mean-field models, since electrons move independently, feeling only the “average electric field” due to the other electrons. These models are also referred to as “independent particle models.” The most famous independent particle model—sometimes called *the* independent particle model—is Hartree-Fock theory, about which we shall have much more to say.

There are many different mean-field approximations, each of which uses a different choice for  $\hat{w}(\mathbf{r})$ . Historically, the most important approximation is the Hartree-Fock model, though Kohn-Sham density functional theory (which also uses Eq. (1.9)) has now supplanted the Hartree-Fock method in many contexts. In the preceding analysis, we have already been introduced to yet another independent-particle model, the Hartree approximation. In the Hartree approximation, the electrons feel the repulsion due to all the other electrons in the system, thus

$$\hat{w}_{\text{Hartree}}(\mathbf{r})\psi_i(\mathbf{r}) = \left( \int \frac{\sum_{k=1}^N |\psi_k(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' - \int \frac{|\psi_i(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' \right) \psi_i(\mathbf{r}). \quad (1.11)$$

Equation (1.4) is just the special case of Eq. (1.11), as applied to a  $2s$  orbital in the 10-electron atom. The first term in Eq. (1.11) is just the electrostatic potential from the electrons in the molecule. Note that sums of the squares of the orbitals,

$$\rho(\mathbf{r}) = \sum_{k=1}^N |\psi_k(\mathbf{r})|^2, \quad (1.12)$$

is just the probability of observing an electron at the point. Thus,  $\rho(\mathbf{r})$  is called the electron density. The potential an electron feels due to the other electrons would be

$$v_J(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' \quad (1.13)$$

except that the orbitals do not interact with themselves. The second term in Eq. (1.11) is called the self-interaction correction. Note that because different orbitals feel different potentials,

$$\hat{w}_{\text{Hartree}}(\mathbf{r})\psi_i(\mathbf{r}) \equiv \left( \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' - \int \frac{|\psi_i(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' \right) \psi_i(\mathbf{r}) \quad (1.14)$$

is an operator, and not simply a function. (Not only this, but unlike most of the operators we encounter in elementary quantum mechanics,  $\hat{w}_{\text{Hartree}}(\mathbf{r})$  is not linear.)

All the independent particle models I know of include the classical electrostatic repulsion between electrons, Eq. (1.13), but differ based on the second term in Eq. (1.14). Some models omit the self-interaction correction; some models include it approximately; some models go beyond simple self-interaction corrections to more fully include the effects of the Pauli exclusion principle; some models go beyond the Pauli exclusion effects and actually include the effects of electron correlation.

## B. The Self-Consistent Field (SCF) Method

screened nuclear charge. That is, we can think about the e

## C. Secular Equations

## D. Basis Sets

## E. The Slater Determinant

We have already been introduced to the Hartree-Fock method, at least in principle. Specifically, we learned that the Hartree Fock method uses a wave function that is a Slater determinant of one-electron orbitals,

$$\begin{aligned} \Phi(\mathbf{r}_1, \sigma(1); \dots; \mathbf{r}_N, \sigma(N)) &\equiv \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\mathbf{r}_1)\sigma_1(1) & \psi_2(\mathbf{r}_1)\sigma_2(1) & \cdots & \psi_N(\mathbf{r}_1)\sigma_N(1) \\ \psi_1(\mathbf{r}_2)\sigma_1(2) & \psi_2(\mathbf{r}_2)\sigma_2(2) & \cdots & \psi_N(\mathbf{r}_2)\sigma_N(2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(\mathbf{r}_N)\sigma_1(N) & \psi_2(\mathbf{r}_N)\sigma_2(N) & \cdots & \psi_N(\mathbf{r}_N)\sigma_N(N) \end{vmatrix} \\ &= \begin{vmatrix} \psi_1\sigma_1 & \psi_2\sigma_2 & \cdots & \psi_N\sigma_N \end{vmatrix}. \end{aligned} \quad (1.15)$$

The  $\frac{1}{\sqrt{N!}}$  normalization factor is only correct when the orbitals are orthonormal, and the second line of Eq. (1.15) is just the “short-hand” notation you have already seen. Since the determinant of a matrix and its transpose are the same, the rows and columns of Eq. (1.15) are often interchanged. (Equation (1.15) is slightly more standard.)

We often introduce short-hand notation for the space+spin coordinates of an electron,  $(\mathbf{r}, \sigma)$  (or  $(\mathbf{r}, s)$ ). For example, sometimes we denote

$$(\mathbf{r}_i, \sigma_i) \rightarrow \mathbf{z}_i \text{ (or } \mathbf{x}_i) \quad (1.16)$$

or just

$$(\mathbf{r}_i, \sigma_i) \rightarrow (i). \quad (1.17)$$

I tend to use the first convention when I’m typing and the second, more compact, notation when I’m writing (on the board or on paper). Orbitals that depend on both spatial and spin coordinates are usually called “spin-orbitals”, while those that depend only on the spatial part are just “orbitals.” But “spin-orbitals” are sometimes called “orbitals” when the spin-dependence is obvious from context.

It is important to recall that “integration” over spin coordinates is defined according to the rule

$$\begin{aligned} \int \psi_i(\mathbf{z}) \psi_j(\mathbf{z}) d\mathbf{z} &= \int \psi_i(\mathbf{r}, s) \psi_j(\mathbf{r}, s) d\mathbf{r} ds \\ &= \int \psi_i(\mathbf{r}) \psi_j(\mathbf{r}) d\mathbf{r} \langle \sigma_i | \sigma_j \rangle \\ &= \delta_{ij} \delta_{\sigma_i \sigma_j} \end{aligned} \quad (1.18)$$

where  $\sigma_i$  denotes the spin wave function ( $\alpha$  or  $\beta$ ) paired to the spatial orbital,  $\phi_i(\mathbf{r})$  of interest. *Note that orbitals with different spins are always orthogonal.* In fact, any time an integrand

includes two electrons with the same “spatial” coordinate but different spin, the integral will be zero.

The gist of the Hartree-Fock method is to find the “best” Slater determinant for approximating the ground-state wave function. What is “best”? There are two reasonable ways to define “best”. First of all, we can take the “best” Slater determinant to be the one with the lowest energy. This gives the Hartree-Fock method as it is usually stated, namely,

$$E_{HF} = \min_{\Phi} \frac{\langle \Phi | \hat{H} | \Phi \rangle}{\langle \Phi | \Phi \rangle} \quad (1.19)$$

which is interpreted as “minimize the energy with respect to all wave functions that are Slater determinants. The minimization in Eq. (1.19) can be performed by minimizing the energy with respect to the orbitals in the Slater determinant,

$$E_{HF} = \min_{\{\psi_i\}_{i=1}^N} \frac{\langle \Phi | \hat{H} | \Phi \rangle}{\langle \Phi | \Phi \rangle}. \quad (1.20)$$

The Hartree-Fock wave function is the Slater determinant for which the minimum value of the energy is achieved. That is, the Hartree-Fock wave function is the argument of the energy functional at the minimum, which we denote,

$$\Phi_{HF} = \arg \min_{\Phi} \frac{\langle \Phi | \hat{H} | \Phi \rangle}{\langle \Phi | \Phi \rangle} \quad (1.21)$$

## F. Digression: Is the Hartree Fock Wave Function Really the “Best” Slater Determinant?

We could also define the “best” wave function to be the one that is the “closest” to the exact wave function. The distance between two wave-functions is usually (though not always) measures in what is called the  $\mathbb{L}^2$  norm,

$$d(\Phi, \Psi) = \sqrt{\langle \Phi - \Psi | \Phi - \Psi \rangle}. \quad (1.22)$$

Let  $\Psi_0$  be the ground state wave function, and  $\{\Psi_k\}_{k=0}^{\infty}$  denote the eigenfunctions (ground and excited state) of the system of interest. Then we can write any Slater determinant as a linear combination of these eigenfunctions,

$$\begin{aligned} \Phi &= \sum_{k=0}^{\infty} \langle \Psi_k | \Phi \rangle \Psi_k \\ &= \sum_{k=0}^{\infty} c_k \Psi_k \end{aligned} \quad (1.23)$$

and, substituting back into Eq. (1.22), we find that

$$\begin{aligned}
d(\Phi, \Psi_0) &= \sqrt{\langle \Phi - \Psi_0 | \Phi - \Psi_0 \rangle} \\
&= \sqrt{\langle \Phi | \Phi \rangle + \langle \Psi_0 | \Psi_0 \rangle - \left\langle \sum_{k=0}^{\infty} c_k \Psi_k \middle| \Psi_0 \right\rangle - \left\langle \Psi_0 \middle| \sum_{j=0}^{\infty} c_j \Psi_j \right\rangle} \\
&= \sqrt{2 - 2 \operatorname{Re}(c_0)} \\
&= \sqrt{2 - 2 \operatorname{Re}(\langle \Phi | \Psi_0 \rangle)}
\end{aligned} \tag{1.24}$$

which is to say that a large overlap between the Slater determinant and the ground state wave function indicates that the wave functions are “close together.” This is very similar to the requirement that the difference in energy between the Hartree-Fock wave function and the exact wave function be small, which is

$$\begin{aligned}
\Delta E &= E_{HF} - E_0 \\
&= (|c_0|^2 - 1)E_0 + \sum_{k=1}^{\infty} |c_k|^2 E_k.
\end{aligned} \tag{1.25}$$

In both cases, it is favorable for the overlap between the Hartree-Fock and the exact wave function to be close to one, but in the Hartree-Fock case, we find that there is also a dependence on the higher-order coefficients. The wave function that satisfies the minimum energy criterion is the usual Hartree-Fock wave function, while the wave function that satisfies the minimum distance criterion is a Slater determinant of the highest-occupied *natural orbitals*. Both wave functions are important, and the two wave functions are almost always very similar to one another. Often it is said that the Hartree-Fock wave function is the “best” Slater determinant wave function in the sense that it is the “closest” to the exact wave function. This is not true: the Hartree-Fock wave function is the “best” wave function insofar as it has the lowest energy. Other Slater determinants are sometimes preferred when describing other properties of the system.

## G. Restricted and Unrestricted Hartree-Fock

Often, motivated by the usual statement of the Pauli exclusion principle: “there can be no more than two electrons in any one orbital” we restrict ourselves to “spin pairs” of orbitals, so that to every  $\alpha$ -spin orbital,  $\psi_i(\mathbf{r})\alpha$ , there is a  $\beta$ -spin orbital,  $\psi_i(\mathbf{r})\beta$ . However, this is not necessary, and sometimes we do not restrict orbitals to be spin-paired, in which case we are using the unrestricted Hartree-Fock method. Note that the unrestricted Hartree-Fock method can give a “restricted” wave function if this minimizes the energy in Eq. (1.19), but the unrestricted Hartree-Fock result can give a lower energy also, because the energy minimization can explore the possibility that the “spatial parts” of two orbitals in a “spin pair” are not the same. Thus

$$E_{UHF} \leq E_{RHF}. \tag{1.26}$$

When is the unrestricted Hartree-Fock (UHF) approach helpful? *If the system exists in a singlet state, the unrestricted and restricted Hartree-Fock methods give the exact same result.* However, when the number of  $\alpha$ -spin electrons is greater than the number of  $\beta$ -spin electrons, the “symmetry” between the two electron channels is broken. Choosing, as is convention,  $\alpha$ -spin as the “majority spin channel”, we see that because  $N_\alpha > N_\beta$ , the  $\alpha$  spin-electrons will be affected more strongly by the Pauli-exclusion principle than the  $\beta$  spin electrons. Insofar as “exchange” interactions are favorable, this gives  $\alpha$ -spin orbitals *slightly* lower energies than their  $\beta$  spin counterparts. Clearly, in this case, because the number of  $\alpha$ -spin electrons is different from the number of  $\beta$ -spin electrons, there are advantages to employing orbitals that are slightly different for

the two different spin-channels. For example, in the Lithium atom, we expect that the  $\alpha$ -spin and  $\beta$ -spin orbitals describing the “1s” state,  $\psi_{1s}^\alpha(\mathbf{r}_1)\alpha(1)$  and  $\psi_{1s}^\beta(\mathbf{r}_1)\beta(1)$ , will have slightly different spatial profiles ( $\psi_{1s}^\alpha(\mathbf{r}) \neq \psi_{1s}^\beta(\mathbf{r})$ ).

Another case where it is helpful to use unrestricted Hartree-Fock calculations is when considering molecular dissociation. Recall that, in conventional molecular orbital theory, the description of the dissociation of molecules (even simple  $H_2$ ) was quite bad. This was due to the restriction that the  $\alpha$ - and  $\beta$ -spin orbitals be identical, which forced the hydrogen molecule’s orbitals to have the form of a sum of the two atomic orbitals centered on the hydrogen atoms:

$$\psi_{H_2}(\mathbf{r}) \equiv (\psi_1(\mathbf{r}-\mathbf{R}_A) + \psi_1(\mathbf{r}-\mathbf{R}_B)). \quad (1.27)$$

But if we use the unrestricted formulation, the orbitals can be taken to be different, giving a molecular orbital with the more general form,

$$\psi_{H_2}^{UHF}(\mathbf{r}) = c\psi_1(\mathbf{r}-\mathbf{R}_A)\alpha + \sqrt{1-c^2}\psi_2(\mathbf{r}-\mathbf{R}_B)\beta. \quad (1.28)$$

Equation (1.28) is the “right” description: when you dissociate the hydrogen molecule, you get two hydrogen atoms, with those atoms having “hydrogen atom” wave functions.

There are also disadvantages to the UHF approach. Most notable is that UHF wave functions are not eigenfunctions of  $\hat{S}^2$ .<sup>6</sup> When the  $\alpha$ -spin orbitals and  $\beta$ -spin orbitals are not identical, the Slater determinant is not an eigenfunction of  $\hat{S}^2$ . Such wave functions are said to be “spin contaminated,” and the obvious remedy is to, just as we did with atoms, choose linear combinations of Slater determinants to describe the “spectroscopic terms.” Such functions are called “symmetry-adapted linear combinations.” An alternative is to force the  $\alpha$ -spin orbitals and  $\beta$ -spin orbitals to have the same spatial part, an approach that is usually called the ROHF method (ROHF = Restricted Open-Shell Hartree-Fock) in systems where electrons are not all paired. The ROHF method is preferable to the restricted-Hartree-Fock approach when no single determinant can describe the spin and/or symmetry (as the angular momentum symmetry reflected in the  $\hat{L}^2$  operator for atoms) of the system.

## H. A Brief Introduction to Hartree-Fock

### I. Electron Correlation and Corrections to Hartree-Fock

The Hartree-Fock method is the basis for most of computational chemistry, and we will spend a lot of time discussing the Hartree-Fock technique and how it is improved. The basic

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<sup>6</sup> This is easily understood by considering a simple example. For example, you can easily demonstrate that the Slater determinant  $\begin{vmatrix} \psi_1\alpha & \psi_2\beta \end{vmatrix}$  is not an eigenfunction of  $\hat{S}^2$  unless  $\psi_1(\mathbf{r}) = \psi_2(\mathbf{r})$ . This is because it is impermissible to consider only the possibility that the  $\alpha$ -spin electron is in orbital  $\psi_1(\mathbf{r})$ ; it is possible that the alternative assignment of electron spins, represented by the Slater determinant  $\begin{vmatrix} \psi_1\beta & \psi_2\alpha \end{vmatrix}$ , holds. There is no reason to favor the first method of assigning electron spins over the second and, indeed, it is the symmetric forms,  $\begin{vmatrix} \psi_1\alpha & \psi_2\beta \end{vmatrix} \pm \begin{vmatrix} \psi_1\beta & \psi_2\alpha \end{vmatrix}$ , that are eigenfunctions of  $\hat{S}^2$ .



mathematical tools will be presented in the next two sections. First of all, looking at Eq. (1.19) it is clear that we need to be able to find an explicit formula for the energy of a Slater determinant. Second, looking at Eq. (1.20), it is clear that we need to be able to calculate how the energy of a Slater determinant changes when we change one (or more) of its composing orbitals.

## 2. Derivation of the Hartree-Fock Method

### I. The Hartree Product

Look back at Eq. (1.20): in order to calculate find the “lowest-energy” Slater determinant, we need to be able to calculate the energy of a Slater determinant. That is, we need to be able to evaluate integrals like

$$E \equiv \left\langle \begin{vmatrix} \psi_1 & \psi_2 & \dots & \psi_N \end{vmatrix} \left| \hat{Q} \right| \begin{vmatrix} \psi_1 & \psi_2 & \dots & \psi_N \end{vmatrix} \right\rangle \quad (2.1)$$

where  $\hat{Q}$  is an operator. The most important cases are the identity operator (for normalization),

$$\hat{I} = 1 \quad (2.2)$$

the kinetic-energy operator,

$$\hat{T} = \sum_{i=1}^N -\frac{\nabla_i^2}{2}, \quad (2.3)$$

the electron-electron repulsion energy operator,

$$\hat{V}_{ee} \equiv \sum_{i=1}^{N-1} \sum_{j=i+1}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (2.4)$$

and the electron-nuclear attraction energy operator,

$$\hat{V}_{ne} \equiv \sum_{i=1}^N v(\mathbf{r}_i) \quad (2.5)$$

where the external potential,  $v(\mathbf{r})$ , in a molecule with  $N_{\text{atom}}$  atoms is

$$v(\mathbf{r}_i) \equiv \sum_{A=1}^{N_{\text{atoms}}} -\frac{Z_A}{|\mathbf{r}_i - \mathbf{R}_A|}. \quad (2.6)$$

We write the total Hamiltonian as a sum of the one-electron and two-electron pieces, namely,

$$\hat{H} \equiv \sum_{i=1}^N \hat{h}(\mathbf{r}_i) + \sum_{i=1}^{N-1} \sum_{j=i+1}^N \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) \quad (2.7)$$

where the electron-electron repulsion between electrons  $i$  and  $j$  is given by

$$\hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) = \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (2.8)$$

and

$$\hat{h}(\mathbf{r}_i) \equiv \hat{t}(\mathbf{r}_i) + v(\mathbf{r}_i) \quad (2.9)$$

is the sum of the kinetic energy operator for electron  $i$ ,

$$\hat{t}(\mathbf{r}_i) = -\frac{1}{2} \nabla_i^2 \quad (2.10)$$

and the external potential which “binds” this electron to the atom,  $v(\mathbf{r}_i)$  (cf. Eq. (2.6)). Don’t worry quite yet if all this notation isn’t clicking—it will become more familiar once it is used, and the parts that are used least are the least important.

In order to evaluate properties of Slater determinants, it is useful to remember what a Slater determinant is: it is simply an “antisymmetric sum” of all the possible ways to distribute electrons in a system. For example,

$$\begin{aligned}
\left| \begin{matrix} \psi_1 & \psi_2 & \psi_3 \end{matrix} \right| &= \frac{1}{\sqrt{3!}} \begin{vmatrix} \psi_1(\mathbf{z}_1) & \psi_2(\mathbf{z}_1) & \psi_3(\mathbf{z}_1) \\ \psi_1(\mathbf{z}_2) & \psi_2(\mathbf{z}_2) & \psi_3(\mathbf{z}_2) \\ \psi_1(\mathbf{z}_3) & \psi_2(\mathbf{z}_3) & \psi_3(\mathbf{z}_3) \end{vmatrix} \\
&= \frac{1}{\sqrt{6}} \begin{pmatrix} \psi_1(\mathbf{z}_1)\psi_2(\mathbf{z}_2)\psi_3(\mathbf{z}_3) \\ \left[ \begin{matrix} \psi_1(\mathbf{z}_2)\psi_2(\mathbf{z}_1)\psi_3(\mathbf{z}_3) \\ +\psi_1(\mathbf{z}_3)\psi_2(\mathbf{z}_2)\psi_3(\mathbf{z}_1) \\ +\psi_1(\mathbf{z}_1)\psi_2(\mathbf{z}_3)\psi_3(\mathbf{z}_2) \end{matrix} \right] \\ -\left[ \begin{matrix} \psi_1(\mathbf{z}_2)\psi_2(\mathbf{z}_3)\psi_3(\mathbf{z}_1) \\ +\psi_1(\mathbf{z}_3)\psi_2(\mathbf{z}_1)\psi_3(\mathbf{z}_2) \end{matrix} \right] \end{pmatrix} \quad (2.11)
\end{aligned}$$

Note the trend: we take the product of the diagonal elements of the Slater determinant, then we do all the “single exchanges” (which get a negative sign by the Pauli antisymmetry principle), and then form all the “unique” double exchanges (which get a positive sign”. The total number of terms is the number of different ways to pick a coordinate for  $\psi_1$  (three),  $\psi_2$  (two), and  $\psi_3$  (one). Each term in Eq. (2.11) is referred to as a Hartree-product wave function, and can be denoted as, for instance,

$$\psi_1(\mathbf{z}_1)\psi_2(\mathbf{z}_2)\psi_3(\mathbf{z}_3) = \left| \begin{matrix} \psi_1 & \psi_2 & \psi_3 \end{matrix} \right| \quad (2.12)$$

So we can write the expression in Eq. (2.11) as:

$$\left| \begin{matrix} \psi_1 & \psi_2 & \psi_3 \end{matrix} \right| = \frac{1}{\sqrt{6}} \begin{pmatrix} |\psi_1\psi_2\psi_3\rangle \\ -|\psi_2\psi_1\psi_3\rangle - |\psi_3\psi_2\psi_1\rangle - |\psi_1\psi_3\psi_2\rangle \\ +|\psi_3\psi_1\psi_2\rangle + |\psi_2\psi_3\psi_1\rangle \end{pmatrix} \quad (2.13)$$

We often find it convenient to denote “exchanges” of coordinates explicitly. We do this by introducing the permutation operator,  $\mathcal{P}_{i,j}$ , which means “exchange the coordinates of orbitals  $i$  and  $j$  in the Hartree product. Thus, Eq. (2.13) becomes

$$\left| \begin{matrix} \psi_1 & \psi_2 & \psi_3 \end{matrix} \right| = \frac{1}{\sqrt{6}} \begin{pmatrix} 1 \\ -\mathcal{P}_{1,2} - \mathcal{P}_{1,3} - \mathcal{P}_{2,3} \\ +\mathcal{P}_{1,2}\mathcal{P}_{2,3} + \mathcal{P}_{1,3}\mathcal{P}_{2,3} \end{pmatrix} |\psi_1\psi_2\psi_3\rangle \quad (2.14)$$

Note that  $\mathcal{P}_{i,j} = \mathcal{P}_{j,i}$  and that the order of permutations does not matter. The Pauli antisymmetry principle indicates that when there are an odd number of permutations, the Hartree product has a negative coefficient.

## II. Integrals of Hartree-Product Wave Functions

Based on the above considerations, it is clear that evaluating integrals between Slater determinants requires merely that we be able to evaluate integrals between Hartree-product wave functions. We have the following results, which are summarized in Table 7.1.

## A. One-electron integrals

### 1. Identical Hartree products, $|\psi_1\psi_2\ldots\psi_N\rangle$ .

$$\begin{aligned}
& \left\langle (\psi_1\psi_2\ldots\psi_N | \hat{h}(\mathbf{r}_i) | \psi_1\psi_2\ldots\psi_N) \right\rangle \\
& \equiv \int \psi_1^*(\mathbf{z}_1)\psi_2^*(\mathbf{z}_2)\cdots\psi_N^*(\mathbf{z}_N) \hat{h}(\mathbf{r}_i) \psi_1(\mathbf{z}_1)\psi_2(\mathbf{z}_2)\cdots\psi_N(\mathbf{z}_N) d\mathbf{z}_1\ldots d\mathbf{z}_N \\
& = \left( \int \psi_1^*(\mathbf{z}_1)\psi_1(\mathbf{z}_1) d\mathbf{z}_1 \cdots \right. \\
& \quad \times \int \psi_{i-1}^*(\mathbf{z}_{i-1})\psi_{i-1}(\mathbf{z}_{i-1}) d\mathbf{r}_{i-1} \int \psi_i^*(\mathbf{z}_i) \hat{h}(\mathbf{r}_i) \psi_i(\mathbf{z}_i) d\mathbf{r}_i \int \psi_{i+1}^*(\mathbf{z}_{i+1})\psi_{i+1}(\mathbf{z}_{i+1}) d\mathbf{z}_{i+1} \cdots \\
& \quad \left. \times \int \psi_N^*(\mathbf{z}_N)\psi_N(\mathbf{z}_N) d\mathbf{z}_N \right) \quad (2.15) \\
& = \langle \psi_i | \hat{h} | \psi_i \rangle \prod_{\substack{k=1 \\ k \neq i}}^N \langle \psi_k | \psi_k \rangle
\end{aligned}$$

Here,  $\prod_{\substack{k=1 \\ k \neq i}}^N \langle \psi_k | \psi_k \rangle$  denotes the product of “normalization integrals” for all the

orbitals except  $\psi_i$ . For example, for four electrons,

$$\left\langle (\psi_1\psi_2\psi_3\psi_4 | \hat{h}(\mathbf{r}_2) | \psi_1\psi_2\psi_3\psi_4) \right\rangle = \langle \psi_2 | \hat{h} | \psi_2 \rangle \langle \psi_1 | \psi_1 \rangle \langle \psi_3 | \psi_3 \rangle \langle \psi_4 | \psi_4 \rangle \quad (2.16)$$

If the orbitals are normalized, then  $\langle \psi_k | \psi_k \rangle = 1$  and

$$\left\langle (\psi_1\psi_2\ldots\psi_N | \hat{h}(\mathbf{r}_i) | \psi_1\psi_2\ldots\psi_N) \right\rangle = \langle \psi_i | \hat{h} | \psi_i \rangle \quad (2.17)$$

### 2. Two Hartree-products differing by the orbital for the $\alpha^{\text{th}}$ electron. That is, the two Hartree products are given by $|\psi_1\ldots\psi_\alpha\ldots\psi_N\rangle$ and $|\psi_1\ldots\psi'_\alpha\ldots\psi_N\rangle$ , where $\psi_\alpha(\mathbf{r}) \neq \psi'_\alpha(\mathbf{r})$ .

There are two cases.

**Case I.** When the one-electron integral operates on an electron,  $i$ , other than electron  $\alpha$ , then the result is a simple generalization of Eq. (2.15):

$$\left\langle (\psi_1\ldots\psi'_\alpha\ldots\psi_N | \hat{h}(\mathbf{r}_i) | \psi_1\ldots\psi_\alpha\ldots\psi_N) \right\rangle = \langle \psi_i | \hat{h} | \psi_i \rangle \langle \psi'_\alpha | \psi_\alpha \rangle \prod_{\substack{k=1 \\ k \neq \alpha \\ k \neq i}}^N \langle \psi_k | \psi_k \rangle \quad (2.18)$$

For example, for four electrons

$$\left\langle (\psi_1\psi_2\psi_3\psi_4 | \hat{h}(\mathbf{r}_1) | \psi_1\psi'_2\psi_3\psi_4) \right\rangle = \langle \psi_1 | \hat{h} | \psi_1 \rangle \langle \psi'_2 | \psi_2 \rangle \langle \psi_3 | \psi_3 \rangle \langle \psi_4 | \psi_4 \rangle \quad (2.19)$$

In the important case where  $\psi_\alpha(\mathbf{r})$  and  $\psi'_\alpha(\mathbf{r})$  are orthogonal (so  $\langle \psi'_\alpha | \psi_\alpha \rangle = 0$ ) then

$$\left\langle (\psi_1\ldots\psi'_\alpha\ldots\psi_N | \hat{h}(\mathbf{r}_i) | \psi_1\ldots\psi_\alpha\ldots\psi_N) \right\rangle = 0 \quad (\alpha \neq i) \quad (2.20)$$

**Case II.** When the one-electron integral operates on electron  $\alpha$ , then a simple generalization of the argument in Equation (2.15) shows that

$$\left\langle \left( \psi_1 \dots \psi'_\alpha \dots \psi_N \right) \left| \hat{h}(\mathbf{r}_\alpha) \right| \psi_1 \dots \psi_\alpha \dots \psi_N \right\rangle = \left\langle \psi'_\alpha \left| \hat{h} \right| \psi_\alpha \right\rangle \prod_{\substack{k=1 \\ k \neq \alpha}}^N \langle \psi_k | \psi_k \rangle \quad (2.21)$$

For example, for four electrons we have that

$$\left\langle \left( \psi_1 \psi_2 \psi_3 \psi_4 \right) \left| \hat{h}(\mathbf{r}_2) \right| \psi_1 \psi'_2 \psi_3 \psi_4 \right\rangle = \left\langle \psi_2 \left| \hat{h} \right| \psi'_2 \right\rangle \langle \psi_1 | \psi_1 \rangle \langle \psi_3 | \psi_3 \rangle \langle \psi_4 | \psi_4 \rangle \quad (2.22)$$

In the important case where the orbitals are all normalized, we have

$$\left\langle \left( \psi_1 \dots \psi'_\alpha \dots \psi_N \right) \left| \hat{h}(\mathbf{r}_\alpha) \right| \psi_1 \dots \psi_\alpha \dots \psi_N \right\rangle = \left\langle \psi'_\alpha \left| \hat{h} \right| \psi_\alpha \right\rangle \quad (2.23)$$

There is no simplification resulting from the assumption that  $\psi_\alpha(\mathbf{r})$  and  $\psi'_\alpha(\mathbf{r})$  are orthogonal.

**3. Two Hartree-products differing by the orbitals for the  $\alpha^{th}$  electron and the orbital for the  $\beta^{th}$  electron. The two Hartree products are given by  $|\psi_1 \dots \psi_\alpha \dots \psi_\beta \dots \psi_N\rangle$  and  $|\psi_1 \dots \psi'_\alpha \dots \psi'_\beta \dots \psi_N\rangle$ , with  $\psi_\alpha(\mathbf{r}) \neq \psi'_\alpha(\mathbf{r})$  and  $\psi_\beta(\mathbf{r}) \neq \psi'_\beta(\mathbf{r})$ .**

There are, as before two cases.

**Case I.** The electron under consideration is neither electron  $\alpha$  nor electron  $\beta$ . Then, similar to Eq. (2.18), we have

$$\left\langle \left( \psi_1 \dots \psi'_\alpha \dots \psi'_\beta \dots \psi_N \right) \left| \hat{h}(\mathbf{r}_i) \right| \psi_1 \dots \psi_\alpha \dots \psi_\beta \dots \psi_N \right\rangle = \left\langle \psi_i \left| \hat{h} \right| \psi_i \right\rangle \langle \psi'_\alpha | \psi_\alpha \rangle \langle \psi'_\beta | \psi_\beta \rangle \prod_{\substack{k=1 \\ k \neq \alpha, \beta, i}}^N \langle \psi_k | \psi_k \rangle \quad (2.24)$$

and if the primed and unprimed orbitals are orthogonal ( $\langle \psi'_\alpha | \psi_\alpha \rangle = \langle \psi'_\beta | \psi_\beta \rangle = 0$ ), then

$$\left\langle \left( \psi_1 \dots \psi'_\alpha \dots \psi'_\beta \dots \psi_N \right) \left| \hat{h}(\mathbf{r}_i) \right| \psi_1 \dots \psi_\alpha \dots \psi_\beta \dots \psi_N \right\rangle = 0 \quad (2.25)$$

**Case II.** The electron under consideration is electron  $\alpha$  (the answer is similar for electron  $\beta$ ). Then

$$\begin{aligned} & \left\langle \left( \psi_1 \dots \psi'_\alpha \dots \psi'_\beta \dots \psi_N \right) \left| \hat{h}(\mathbf{r}_\alpha) \right| \psi_1 \dots \psi_\alpha \dots \psi_\beta \dots \psi_N \right\rangle \\ &= \left\langle \psi'_\alpha \left| \hat{h} \right| \psi_\alpha \right\rangle \langle \psi'_\beta | \psi_\beta \rangle \prod_{\substack{k=1 \\ k \neq \alpha, \beta}}^N \langle \psi_k | \psi_k \rangle \end{aligned} \quad (2.26)$$

and in the important case where the primed and unprimed orbitals are orthogonal ( $\langle \psi'_\alpha | \psi_\alpha \rangle = \langle \psi'_\beta | \psi_\beta \rangle = 0$ ), then

$$\left\langle \left( \psi_1 \dots \psi'_\alpha \dots \psi'_\beta \dots \psi_N \right) \left| \hat{h}(\mathbf{r}_\alpha) \right| \psi_1 \dots \psi_\alpha \dots \psi_\beta \dots \psi_N \right\rangle = 0 \quad (2.27)$$

4. For Hartree products differing by more than two orbitals, the one-electron integrals are zero as long as different orbitals are orthogonal.

## B. for two-electron integrals.

### 1. Identical Hartree-products, $|\psi_1\psi_2\ldots\psi_N\rangle$ .

$$\begin{aligned}
& \left\langle (\psi_1\psi_2\ldots\psi_N | \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) | \psi_1\psi_2\ldots\psi_N) \right\rangle \\
& \equiv \int \psi_1^*(\mathbf{z}_1)\psi_2^*(\mathbf{z}_2)\cdots\psi_N^*(\mathbf{z}_N) \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) \psi_1(\mathbf{z}_1)\psi_2(\mathbf{z}_2)\cdots\psi_N(\mathbf{z}_N) d\mathbf{z}_1 \ldots d\mathbf{z}_N \\
& = \left( \int \psi_1^*(\mathbf{r}_1)\psi_1(\mathbf{r}_1) d\mathbf{r}_1 \ldots \right. \\
& \quad \times \int \psi_{i-1}^*(\mathbf{z}_{i-1})\psi_{i-1}(\mathbf{z}_{i-1}) d\mathbf{z}_{i-1} \left( \int \psi_i^*(\mathbf{z}_i)\psi_j^*(\mathbf{z}_j) \hat{v}_{ee}(\mathbf{z}_i, \mathbf{z}_j) \psi_j(\mathbf{z}_j)\psi_i(\mathbf{z}_i) d\mathbf{z}_i d\mathbf{z}_j \right) \\
& \quad \times \int \psi_{i+1}^*(\mathbf{z}_{i+1})\psi_{i+1}(\mathbf{z}_{i+1}) d\mathbf{z}_{i+1} \cdots \\
& \quad \times \int \psi_{j-1}^*(\mathbf{z}_{j-1})\psi_{j-1}(\mathbf{z}_{j-1}) d\mathbf{r}_{j-1} \int \psi_{j+1}^*(\mathbf{z}_{j+1})\psi_{j+1}(\mathbf{z}_{j+1}) d\mathbf{z}_{j+1} \cdots \\
& \quad \left. \times \int \psi_N^*(\mathbf{z}_N)\psi_N(\mathbf{z}_N) d\mathbf{z}_N \right) \quad (2.28) \\
& = \left\langle (\psi_i\psi_j | \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) | \psi_i\psi_j) \right\rangle \prod_{\substack{k=1 \\ k \neq i, j}}^N \langle \psi_k | \psi_k \rangle
\end{aligned}$$

For example, for five electrons,

$$\left\langle (\psi_1\psi_2\psi_3\psi_4\psi_5 | \hat{v}_{ee}(\mathbf{r}_2, \mathbf{r}_4) | \psi_1\psi_2\psi_3\psi_4\psi_5) \right\rangle = \langle \psi_2\psi_4 | \hat{v}_{ee} | \psi_2\psi_4 \rangle \langle \psi_1 | \psi_1 \rangle \langle \psi_3 | \psi_3 \rangle \langle \psi_5 | \psi_5 \rangle \quad (2.29)$$

Notice the introduction of a useful “shorthand” for the integrals in Eq. (2.29). It is understood that

$$\langle \psi_i\psi_j | \hat{v}_{ee} | \psi_i\psi_j \rangle \equiv \left\langle \psi_i(\mathbf{z}_i)\psi_j(\mathbf{z}_j) | \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) | \psi_i(\mathbf{z}_i)\psi_j(\mathbf{z}_j) \right\rangle. \quad (2.30)$$

If the orbitals are normalized, then  $\langle \psi_k | \psi_k \rangle = 1$  and

$$\left\langle (\psi_1\psi_2\ldots\psi_N | \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) | \psi_1\psi_2\ldots\psi_N) \right\rangle = \left\langle (\psi_i\psi_j | \hat{v}_{ee} | \psi_i\psi_j) \right\rangle \quad (2.31)$$

2. Two Hartree-products differing by the orbital for the  $\alpha^{\text{th}}$  electron. That is, the two Hartree products are given by  $|\psi_1\ldots\psi_\alpha\ldots\psi_N\rangle$  and  $|\psi_1\ldots\psi'_\alpha\ldots\psi_N\rangle$ , where  $\psi_\alpha(\mathbf{r}) \neq \psi'_\alpha(\mathbf{r})$ .

There are two cases.

**Case I.** When the electron-electron repulsion operator does not operate on electron  $\alpha$ . Then, generalizing Eq. (2.28), we see that

$$\left\langle (\psi_1\ldots\psi'_\alpha\ldots\psi_N | \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) | \psi_1\ldots\psi_\alpha\ldots\psi_N) \right\rangle = \left\langle (\psi_i\psi_j | \hat{v}_{ee} | \psi_i\psi_j) \right\rangle \langle \psi'_\alpha | \psi_\alpha \rangle \prod_{\substack{k=1 \\ k \neq i, j, \alpha}}^N \langle \psi_k | \psi_k \rangle \quad (2.32)$$

Returning to our 5-electron example,

$$\left\langle (\psi_1\psi_2\psi'_3\psi_4\psi_5 | \hat{v}_{ee}(\mathbf{r}_2, \mathbf{r}_4) | \psi_1\psi_2\psi_3\psi_4\psi_5) \right\rangle = \langle \psi_2\psi_4 | \hat{v}_{ee} | \psi_2\psi_4 \rangle \langle \psi'_3 | \psi_3 \rangle \langle \psi_1 | \psi_1 \rangle \langle \psi_5 | \psi_5 \rangle. \quad (2.33)$$

In the important case where  $\psi_\alpha(\mathbf{r})$  and  $\psi'_\alpha(\mathbf{r})$  are orthogonal (so  $\langle \psi'_\alpha | \psi_\alpha \rangle = 0$ ) then

$$\left\langle \left( \psi_1 \dots \psi'_\alpha \dots \psi_N \right) \left| \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) \right| \psi_1 \dots \psi_\alpha \dots \psi_N \right\rangle = 0 \quad \alpha \neq i, j \quad (2.34)$$

**Case II.** When the electron-electron repulsion energy of electron  $\alpha$  is being considered, then a simple generalization of the argument in Equation (2.28) shows that

$$\left\langle \left( \psi_1 \dots \psi'_\alpha \dots \psi_N \right) \left| \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_\alpha) \right| \psi_1 \dots \psi_\alpha \dots \psi_N \right\rangle = \left\langle \left( \psi_i \psi'_\alpha \right) \left| \hat{v}_{ee} \right| \psi_i \psi_\alpha \right\rangle \prod_{\substack{k=1 \\ k \neq i, \alpha}}^N \langle \psi_k | \psi_k \rangle \quad (2.35)$$

For example, for four electrons we have that

$$\left\langle \left( \psi_1 \psi_2 \psi_3 \psi'_4 \right) \left| \hat{v}_{ee}(\mathbf{r}_2, \mathbf{r}_4) \right| \psi_1 \psi_2 \psi_3 \psi_4 \right\rangle = \langle \psi_2 \psi'_4 | \hat{v}_{ee} | \psi_2 \psi_4 \rangle \langle \psi_3 | \psi_3 \rangle \langle \psi_1 | \psi_1 \rangle \langle \psi_5 | \psi_5 \rangle \quad (2.36)$$

In the important case where the orbitals are all normalized, we have

$$\left\langle \left( \psi_1 \dots \psi'_\alpha \dots \psi_N \right) \left| \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_\alpha) \right| \psi_1 \dots \psi_\alpha \dots \psi_N \right\rangle = \langle \psi_i \psi'_\alpha | \hat{v}_{ee} | \psi_i \psi_\alpha \rangle \quad (2.37)$$

No simplification results from the assumption that  $\psi_\alpha(\mathbf{r})$  and  $\psi'_\alpha(\mathbf{r})$  are orthogonal.

**3. Two Hartree-products differing by the orbitals for the  $\alpha^{th}$  electron and the orbital for the  $\beta^{th}$  electron. The two Hartree products are given by  $|\psi_1 \dots \psi_\alpha \dots \psi_\beta \dots \psi_N\rangle$  and  $|\psi_1 \dots \psi'_\alpha \dots \psi'_\beta \dots \psi_N\rangle$ , with  $\psi_\alpha(\mathbf{r}) \neq \psi'_\alpha(\mathbf{r})$  and  $\psi_\beta(\mathbf{r}) \neq \psi'_\beta(\mathbf{r})$ .**

There are three cases.

**Case I.** The electron-electron repulsion operator does not include the coordinates for electron  $\alpha$  or the coordinates for electron  $\beta$ . Then,

$$\begin{aligned} & \left\langle \left( \psi_1 \dots \psi'_\alpha \dots \psi'_\beta \dots \psi_N \right) \left| \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) \right| \psi_1 \dots \psi_\alpha \dots \psi_\beta \dots \psi_N \right\rangle \\ &= \left\langle \left( \psi_i \psi_j \right) \left| \hat{v}_{ee} \right| \psi_i \psi_j \right\rangle \langle \psi'_\alpha | \psi_\alpha \rangle \langle \psi'_\beta | \psi_\beta \rangle \prod_{\substack{k=1 \\ k \neq i, j, \alpha, \beta}}^N \langle \psi_k | \psi_k \rangle \end{aligned} \quad (2.38)$$

and if the primed and unprimed orbitals are orthogonal ( $\langle \psi'_\alpha | \psi_\alpha \rangle = \langle \psi'_\beta | \psi_\beta \rangle = 0$ ), then

$$\left\langle \left( \psi_1 \dots \psi'_\alpha \dots \psi'_\beta \dots \psi_N \right) \left| \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) \right| \psi_1 \dots \psi_\alpha \dots \psi_\beta \dots \psi_N \right\rangle = 0 \quad (2.39)$$

**Case II.** The electron-electron repulsion between electron  $i$  ( $i \neq \beta$ ) and electron  $\alpha$  is being considered. (The situation is similar when we replace the roles of electrons  $\alpha$  and  $\beta$ .) Then

$$\begin{aligned} & \left\langle \left( \psi_1 \dots \psi'_\alpha \dots \psi'_\beta \dots \psi_N \right) \left| \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_\alpha) \right| \psi_1 \dots \psi_\alpha \dots \psi_\beta \dots \psi_N \right\rangle \\ &= \langle \psi_i \psi'_\alpha | \hat{v}_{ee} | \psi_i \psi_\alpha \rangle \langle \psi'_\beta | \psi_\beta \rangle \prod_{\substack{k=1 \\ k \neq i, \alpha, \beta}}^N \langle \psi_k | \psi_k \rangle \end{aligned} \quad (2.40)$$

and in the important case where the primed and unprimed orbitals are orthogonal ( $\langle \psi'_\alpha | \psi_\alpha \rangle = \langle \psi'_\beta | \psi_\beta \rangle = 0$ ), then

$$\left\langle \left( \psi_1 \dots \psi'_\alpha \dots \psi'_\beta \dots \psi_N \right) \left| \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_\alpha) \right| \psi_1 \dots \psi_\alpha \dots \psi_\beta \dots \psi_N \right\rangle = 0 \quad i \neq \beta \quad (2.41)$$

**Case III.** The electron-electron repulsion between electrons  $\alpha$  and electrons  $\beta$  is being considered. Then,

$$\begin{aligned} \int_{-\infty}^{\infty} \frac{e^{i\omega t}}{(\omega - \omega_k)} d\omega &= e^{i\omega_k t} \int_{-\infty}^{\infty} \frac{e^{i(\omega - \omega_k)t}}{\omega - \omega_k} d\omega \\ &= e^{i\omega_k t} \int_{-\infty}^{\infty} \frac{e^{i(\omega - \omega_k)t}}{\omega - \omega_k} d(\omega - \omega_0) \\ &= e^{i\omega_k t} \left( \frac{-1}{2i} \right) \text{sgn}(t) \\ &= \frac{i}{2} e^{i\omega_k t} \text{sgn}(t). \end{aligned} \quad (2.42)$$

and in the important case where the orbitals are normalized, then

$$\left\langle \left( \psi_1 \dots \psi'_\alpha \dots \psi'_\beta \dots \psi_N \right) \left| \hat{v}_{ee}(\mathbf{r}_\alpha, \mathbf{r}_\beta) \right| \psi_1 \dots \psi_\alpha \dots \psi_\beta \dots \psi_N \right\rangle = \left\langle \left( \psi'_\alpha \psi'_\beta \right) \left| \hat{v}_{ee} \right| \psi_\alpha \psi_\beta \right\rangle \quad (2.43)$$

No simplification is obtained by assuming the primed and unprimed orbitals to be orthogonal.

4. **For Hartree products differing by more than two orbitals, the two-electron integrals are zero as long as different orbitals are orthogonal.**



**Table 7.1: Integrals Between Hartree-Product Wave-Functions.**

# of different orbitals	a. Operator	General Result	Orthonormal Orbitals
			0
			0
			0
			0
			0
			0
3 or more		(more complicated, but similar)	0
3 or more		(more complicated, but similar)	0

Using the results in the previous table, we can now construct the integrals for more complicated operators, notably the sums of the 1-electron and 2-electron operators. We have the following key results

## C. Sums of One-Electron Operators

### 1. Identical Hartree products, $|\psi_1\psi_2\ldots\psi_N\rangle$ .

$$\begin{aligned} \left\langle \left( \psi_1\psi_2\ldots\psi_N \left| \sum_{i=1}^N \hat{h}(\mathbf{r}_i) \right| \psi_1\psi_2\ldots\psi_N \right) \right\rangle &\equiv \sum_{i=1}^N \left\langle \psi_i \left| \hat{h} \right| \psi_i \right\rangle \left( \prod_{\substack{k=1 \\ k \neq i}}^N \langle \psi_k | \psi_k \rangle \right) \\ &\stackrel{\text{orthonormal}}{=} \sum_{i=1}^N \left\langle \psi_i \left| \hat{h} \right| \psi_i \right\rangle \end{aligned} \quad (2.44)$$

### 2. Two Hartree products differing by the orbital for the $\alpha^{th}$ electron. That is, the two Hartree products are given by $|\psi_1\ldots\psi_\alpha\ldots\psi_N\rangle$ and $|\psi_1\ldots\psi'_\alpha\ldots\psi_N\rangle$ , where $\psi_\alpha(\mathbf{r}) \neq \psi'_\alpha(\mathbf{r})$ .

$$\begin{aligned} &\left\langle \left( \psi_1\ldots\psi'_\alpha\ldots\psi_N \left| \sum_{i=1}^N \hat{h}(\mathbf{r}_i) \right| \psi_1\ldots\psi_\alpha\ldots\psi_N \right) \right\rangle \\ &= \left\langle \left( \psi_1\ldots\psi'_\alpha\ldots\psi_N \left| \hat{h}(\mathbf{r}_\alpha) \right| \psi_1\ldots\psi_\alpha\ldots\psi_N \right) \right\rangle + \sum_{\substack{i=1 \\ i \neq \alpha}}^N \left\langle \left( \psi_1\ldots\psi'_\alpha\ldots\psi_N \left| \hat{h}(\mathbf{r}_i) \right| \psi_1\ldots\psi_\alpha\ldots\psi_N \right) \right\rangle \\ &= \left\langle \psi'_\alpha \left| \hat{h} \right| \psi_\alpha \right\rangle \prod_{\substack{k=1 \\ k \neq \alpha}}^N \langle \psi_k | \psi_k \rangle + \sum_{i=1}^N \left\langle \psi_i \left| \hat{h} \right| \psi_i \right\rangle \langle \psi'_\alpha | \psi_\alpha \rangle \prod_{\substack{k=1 \\ k \neq \alpha \\ k \neq i}}^N \langle \psi_k | \psi_k \rangle \\ &\stackrel{\text{orthonormal}}{=} \left\langle \psi'_\alpha \left| \hat{h} \right| \psi_\alpha \right\rangle \end{aligned} \quad (2.45)$$

3. **Two Hartree products differing by the orbitals for the  $\alpha^{th}$  electron and the orbital for the  $\beta^{th}$  electron. The two Hartree products are given by  $|\psi_1 \dots \psi_\alpha \dots \psi_\beta \dots \psi_N\rangle$  and  $|\psi_1 \dots \psi'_\alpha \dots \psi'_\beta \dots \psi_N\rangle$ , with  $\psi_\alpha(\mathbf{r}) \neq \psi'_\alpha(\mathbf{r})$  and  $\psi_\beta(\mathbf{r}) \neq \psi'_\beta(\mathbf{r})$ .**

$$\begin{aligned}
& \left\langle \left( \psi_1 \dots \psi'_\alpha \dots \psi'_\beta \dots \psi_N \left| \sum_{i=1}^N \hat{h}(\mathbf{r}_i) \right| \psi_1 \dots \psi_\alpha \dots \psi_\beta \dots \psi_N \right) \right\rangle \\
&= \left\langle \left( \psi_1 \dots \psi'_\alpha \dots \psi'_\beta \dots \psi_N \left| \hat{h}(\mathbf{r}_\alpha) \right| \psi_1 \dots \psi_\alpha \dots \psi_\beta \dots \psi_N \right) \right\rangle \\
&\quad + \left\langle \left( \psi_1 \dots \psi'_\alpha \dots \psi'_\beta \dots \psi_N \left| \hat{h}(\mathbf{r}_\beta) \right| \psi_1 \dots \psi_\alpha \dots \psi_\beta \dots \psi_N \right) \right\rangle \\
&\quad + \sum_{\substack{i=1 \\ i \neq \alpha, \beta}}^N \left\langle \left( \psi_1 \dots \psi'_\alpha \dots \psi'_\beta \dots \psi_N \left| \hat{h}(\mathbf{r}_i) \right| \psi_1 \dots \psi_\alpha \dots \psi_\beta \dots \psi_N \right) \right\rangle \\
&= \left( \langle \psi'_\alpha | \hat{h} | \psi_\alpha \rangle \langle \psi'_\beta | \psi_\beta \rangle + \langle \psi'_\beta | \hat{h} | \psi_\beta \rangle \langle \psi'_\alpha | \psi_\alpha \rangle \right) \left( \prod_{\substack{k=1 \\ k \neq \alpha, \beta, i}}^N \langle \psi_k | \psi_k \rangle \right) \\
&\quad + \sum_{\substack{i=1 \\ i \neq \alpha, \beta}}^N \langle \psi_i | \hat{h} | \psi_i \rangle \langle \psi'_\alpha | \psi_\alpha \rangle \langle \psi'_\beta | \psi_\beta \rangle \prod_{\substack{k=1 \\ k \neq \alpha, \beta, i}}^N \langle \psi_k | \psi_k \rangle \\
&\stackrel{\text{orthonormal}}{\text{orbitals}} = 0
\end{aligned} \tag{2.46}$$

4. **For orthonormal orbitals, sums of one-electron integrals of Hartree-product wave functions differing by three or more orbitals are also zero.**

## D. Sums of Two-Electron Operators

1. **Identical Hartree-products,  $|\psi_1 \psi_2 \dots \psi_N\rangle$ .**

$$\begin{aligned}
& \left\langle \left( \psi_1 \psi_2 \dots \psi_N \left| \sum_{i=1}^{N-1} \sum_{j=i+1}^N \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) \right| \psi_1 \psi_2 \dots \psi_N \right) \right\rangle = \sum_{i=1}^{N-1} \sum_{j=i+1}^N \left\langle \left( \psi_i \psi_j \left| \hat{v}_{ee} \right| \psi_i \psi_j \right) \right\rangle \prod_{\substack{k=1 \\ k \neq i, j}}^N \langle \psi_k | \psi_k \rangle \\
&\stackrel{\text{orthonormal}}{\text{orbitals}} = \sum_{i=1}^{N-1} \sum_{j=i+1}^N \left\langle \left( \psi_i \psi_j \left| \hat{v}_{ee} \right| \psi_i \psi_j \right) \right\rangle
\end{aligned} \tag{2.47}$$

**2. Two Hartree-products differing by the orbital for the  $\alpha^{th}$  electron.**  
**That is, the two Hartree products are given by  $|\psi_1 \dots \psi_\alpha \dots \psi_N\rangle$  and  $|\psi_1 \dots \psi'_\alpha \dots \psi_N\rangle$ , where  $\psi_\alpha(\mathbf{r}) \neq \psi'_\alpha(\mathbf{r})$ .**

$$\begin{aligned}
& \left\langle \left( \psi_1 \dots \psi'_\alpha \dots \psi_N \left| \sum_{i=1}^{N-1} \sum_{j=i+1}^N \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) \right| \psi_1 \dots \psi_\alpha \dots \psi_N \right) \right\rangle \\
&= \left\langle \left( \psi_1 \dots \psi'_\alpha \dots \psi_N \left| \sum_{i=1}^{\alpha-1} \sum_{\substack{j=i+1 \\ j \neq \alpha}}^N \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) \right| \psi_1 \dots \psi_\alpha \dots \psi_N \right) \right\rangle \\
&\quad + \left\langle \left( \psi_1 \dots \psi'_\alpha \dots \psi_N \left| \sum_{i=1}^{\alpha-1} \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_\alpha) \right| \psi_1 \dots \psi_\alpha \dots \psi_N \right) \right\rangle \\
&\quad + \left\langle \left( \psi_1 \dots \psi'_\alpha \dots \psi_N \left| \sum_{j=\alpha+1}^N \hat{v}_{ee}(\mathbf{r}_\alpha, \mathbf{r}_j) \right| \psi_1 \dots \psi_\alpha \dots \psi_N \right) \right\rangle \\
&\quad + \left\langle \left( \psi_1 \dots \psi'_\alpha \dots \psi_N \left| \sum_{i=\alpha+1}^{N-1} \sum_{j=i+1}^N \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) \right| \psi_1 \dots \psi_\alpha \dots \psi_N \right) \right\rangle \\
&= \left\langle \left( \psi_1 \dots \psi'_\alpha \dots \psi_N \left| \sum_{i=1}^{\alpha-1} \sum_{\substack{j=i+1 \\ j \neq \alpha}}^N \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) \right| \psi_1 \dots \psi_\alpha \dots \psi_N \right) \right\rangle \\
&\quad + \left\langle \left( \psi_1 \dots \psi'_\alpha \dots \psi_N \left| \sum_{i=1}^{\alpha+1} \sum_{j=i+1}^N \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) \right| \psi_1 \dots \psi_\alpha \dots \psi_N \right) \right\rangle \\
&\quad + \sum_{\substack{i=1 \\ i \neq \alpha}}^N \left\langle \left( \psi_1 \dots \psi'_\alpha \dots \psi_N \left| \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_\alpha) \right| \psi_1 \dots \psi_\alpha \dots \psi_N \right) \right\rangle \\
&= \sum_{\substack{i=1 \\ i \neq \alpha}}^{N-1} \sum_{\substack{j=i+1 \\ j \neq \alpha}}^N \left\langle \left( \psi_i \psi_j \left| \hat{v}_{ee} \right| \psi_i \psi_j \right) \right\rangle \langle \psi'_\alpha | \psi_\alpha \rangle \prod_{\substack{k=1 \\ k \neq i, j, \alpha}}^N \langle \psi_k | \psi_k \rangle \\
&\quad + \sum_{\substack{i=1 \\ i \neq \alpha}}^N \left\langle \left( \psi_i \psi'_\alpha \left| \hat{v}_{ee} \right| \psi_i \psi_\alpha \right) \right\rangle \prod_{\substack{k=1 \\ k \neq i, \alpha}}^N \langle \psi_k | \psi_k \rangle \\
&\stackrel{\text{orthonormal}}{\text{orbitals}} = \sum_{\substack{i=1 \\ i \neq \alpha}}^N \left\langle \left( \psi_i \psi'_\alpha \left| \hat{v}_{ee} \right| \psi_i \psi_\alpha \right) \right\rangle
\end{aligned} \tag{2.48}$$

3. **Two Hartree products differing by the orbitals for the  $\alpha^{th}$  electron and the orbital for the  $\beta^{th}$  electron. The two Hartree products are given by  $|\psi_1 \dots \psi_\alpha \dots \psi_\beta \dots \psi_N\rangle$  and  $|\psi_1 \dots \psi'_\alpha \dots \psi'_\beta \dots \psi_N\rangle$ , with  $\psi_\alpha(\mathbf{r}) \neq \psi'_\alpha(\mathbf{r})$  and  $\psi_\beta(\mathbf{r}) \neq \psi'_\beta(\mathbf{r})$ .**

$$\begin{aligned}
& \left\langle \left( \psi_1 \dots \psi'_\alpha \dots \psi'_\beta \dots \psi_N \left| \sum_{i=1}^{N-1} \sum_{j=i+1}^N \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) \right| \psi_1 \dots \psi_\alpha \dots \psi_\beta \dots \psi_N \right) \right\rangle \\
&= \sum_{\substack{i=1 \\ i \neq \alpha, \beta}}^{N-1} \sum_{\substack{j=i+1 \\ j \neq \alpha, \beta}}^N \left\langle (\psi_i \psi_j | \hat{v}_{ee} | \psi_i \psi_j) \right\rangle \langle \psi'_\alpha | \psi_\alpha \rangle \langle \psi'_\beta | \psi_\beta \rangle \prod_{\substack{k=1 \\ k \neq i, j, \alpha, \beta}}^N \langle \psi_k | \psi_k \rangle \\
&\quad + \sum_{\substack{i=1 \\ i \neq \alpha, \beta}}^N \left( \left\langle (\psi_i \psi'_\alpha | \hat{v}_{ee} | \psi_i \psi_\alpha) \right\rangle \langle \psi'_\beta | \psi_\beta \rangle \right) \left( \prod_{\substack{k=1 \\ k \neq i, \alpha, \beta}}^N \langle \psi_k | \psi_k \rangle \right) \\
&\quad + \left\langle (\psi'_\alpha \psi'_\beta | \hat{v}_{ee} | \psi_\alpha \psi_\beta) \right\rangle \prod_{\substack{k=1 \\ k \neq \alpha, \beta}}^N \langle \psi_k | \psi_k \rangle \\
&\stackrel{\text{orthonormal}}{\text{orbitals}} = \left\langle (\psi'_\alpha \psi'_\beta | \hat{v}_{ee} | \psi_\alpha \psi_\beta) \right\rangle
\end{aligned} \tag{2.49}$$

4. **For orthonormal orbitals, sums of two-electron integrals of Hartree-product wave functions differing by three or more orbitals are also zero.**

While the preceding analysis is tedious, it is not difficult. An important point to remember is that, for orthonormal orbitals, the integral will vanish if the number of “different orbitals” is greater than the number of electrons the operator acts on. This is obvious on “intuitive” grounds, since if the operator links  $k$  electrons, then if there are more than  $k$  different orbitals there will be at least one set of orthogonal orbitals,  $\psi'_\lambda(\mathbf{z})$  and  $\psi_\lambda(\mathbf{z})$ , that are not “operated on”, and the presence of a factor of  $\langle \psi'_\lambda | \psi_\lambda \rangle = 0$  renders the expression zero.

**Table: Integrals Between Hartree-Product Wave-Functions and Many-Electron Operators.**

# of different orbitals	a. Operator	General Result	Orthonormal Orbitals
		Eq. (2.44)	
		Eq. (2.47)	
		Eq. (2.45)	
		Eq. (2.48)	
		Eq. (2.46)	<b>0</b>
		Eq. (2.49)	
3 or more		(more complicated, but similar)	<b>0</b>
3 or more		(more complicated, but similar)	<b>0</b>

### III. One-Electron Integrals Between Slater Determinants

We are now, at long last, ready to compute the energy of a Slater determinant. We'll start with a simple example, and then more to the general case. For three electrons, we had (cf. Eq. (2.14))

$$\begin{vmatrix} \psi_1 & \psi_2 & \psi_3 \end{vmatrix} = \frac{1}{\sqrt{6}} \begin{pmatrix} 1 \\ -\mathcal{P}_{1,2} - \mathcal{P}_{1,3} - \mathcal{P}_{2,3} \\ +\mathcal{P}_{1,2}\mathcal{P}_{2,3} + \mathcal{P}_{1,3}\mathcal{P}_{2,3} \end{pmatrix} |\psi_1\psi_2\psi_3\rangle \quad (2.50)$$

and so

$$\begin{aligned} & \left\langle \begin{vmatrix} \psi_1\psi_2\psi_3 \end{vmatrix} \left| \sum_{i=1}^3 \hat{h}(\mathbf{r}_i) \right| \begin{vmatrix} \psi_1\psi_2\psi_3 \end{vmatrix} \right\rangle \\ &= \frac{1}{6} \left\langle \begin{pmatrix} 1 \\ -\mathcal{P}_{1,2} - \mathcal{P}_{1,3} - \mathcal{P}_{2,3} \\ +\mathcal{P}_{1,2}\mathcal{P}_{2,3} + \mathcal{P}_{1,3}\mathcal{P}_{2,3} \end{pmatrix} \begin{vmatrix} \psi_1\psi_2\psi_3 \end{vmatrix} \left| \sum_{i=1}^3 \hat{h}(\mathbf{r}_i) \right| \begin{pmatrix} 1 \\ -\mathcal{P}_{1,2} - \mathcal{P}_{1,3} - \mathcal{P}_{2,3} \\ +\mathcal{P}_{1,2}\mathcal{P}_{2,3} + \mathcal{P}_{1,3}\mathcal{P}_{2,3} \end{pmatrix} \begin{vmatrix} \psi_1\psi_2\psi_3 \end{vmatrix} \right\rangle \end{aligned} \quad (2.51)$$

To understand the result, we need only note that every time one permutes two coordinates the new Hartree-product differs from the original Hartree product by two orbitals. Since the orbitals are orthonormal, both single permutations

$$\left\langle \begin{pmatrix} \psi_1\psi_2\psi_3 \end{pmatrix} \left| \sum_{i=1}^3 \hat{h}(\mathbf{r}_i) \mathcal{P}_{1,2} \right| \begin{pmatrix} \psi_1\psi_2\psi_3 \end{pmatrix} \right\rangle = \left\langle \begin{pmatrix} \psi_1\psi_2\psi_3 \end{pmatrix} \left| \sum_{i=1}^3 \hat{h}(\mathbf{r}_i) \right| \begin{pmatrix} \psi_2\psi_1\psi_3 \end{pmatrix} \right\rangle = 0 \quad (2.52)$$

and double permutations

$$\left\langle \begin{pmatrix} \psi_1\psi_2\psi_3 \end{pmatrix} \left| \sum_{i=1}^3 \hat{h}(\mathbf{r}_i) \mathcal{P}_{1,2}\mathcal{P}_{2,3} \right| \begin{pmatrix} \psi_1\psi_2\psi_3 \end{pmatrix} \right\rangle = \left\langle \begin{pmatrix} \psi_1\psi_2\psi_3 \end{pmatrix} \left| \sum_{i=1}^3 \hat{h}(\mathbf{r}_i) \right| \begin{pmatrix} \psi_2\psi_3\psi_1 \end{pmatrix} \right\rangle = 0 \quad (2.53)$$

are zero. It follows that all the “cross terms” between the permutations in Eq. (2.51) vanish, and one is left with

$$\begin{aligned}
& \left\langle \left| \psi_1 \psi_2 \psi_3 \right| \left| \sum_{i=1}^3 \hat{h}(\mathbf{r}_i) \right| \left| \psi_1 \psi_2 \psi_3 \right| \right\rangle \\
&= \frac{1}{6} \left( \left\langle \left| \psi_1 \psi_2 \psi_3 \right| \left| \sum_{i=1}^3 \hat{h}(\mathbf{r}_i) \right| \left| \psi_1 \psi_2 \psi_3 \right| \right\rangle \right. \\
&\quad + (-1)^2 \left\langle \mathcal{P}_{1,2} \left| \psi_1 \psi_2 \psi_3 \right| \left| \sum_{i=1}^3 \hat{h}(\mathbf{r}_i) \right| \mathcal{P}_{1,2} \left| \psi_1 \psi_2 \psi_3 \right| \right\rangle \\
&\quad + (-1)^2 \left\langle \mathcal{P}_{1,3} \left| \psi_1 \psi_2 \psi_3 \right| \left| \sum_{i=1}^3 \hat{h}(\mathbf{r}_i) \right| \mathcal{P}_{1,3} \left| \psi_1 \psi_2 \psi_3 \right| \right\rangle \\
&\quad + (-1)^2 \left\langle \mathcal{P}_{2,3} \left| \psi_1 \psi_2 \psi_3 \right| \left| \sum_{i=1}^3 \hat{h}(\mathbf{r}_i) \right| \mathcal{P}_{2,3} \left| \psi_1 \psi_2 \psi_3 \right| \right\rangle \\
&\quad + \left\langle \mathcal{P}_{1,2} \mathcal{P}_{2,3} \left| \psi_1 \psi_2 \psi_3 \right| \left| \sum_{i=1}^3 \hat{h}(\mathbf{r}_i) \right| \mathcal{P}_{1,2} \mathcal{P}_{2,3} \left| \psi_1 \psi_2 \psi_3 \right| \right\rangle \\
&\quad \left. + \left\langle \mathcal{P}_{1,3} \mathcal{P}_{2,3} \left| \psi_1 \psi_2 \psi_3 \right| \left| \sum_{i=1}^3 \hat{h}(\mathbf{r}_i) \right| \mathcal{P}_{1,3} \mathcal{P}_{2,3} \left| \psi_1 \psi_2 \psi_3 \right| \right\rangle \right) \quad (2.54)
\end{aligned}$$

However, because the operator,  $\sum_{i=1}^N h(\mathbf{r}_i)$  is symmetric with respect to permutations of the coordinates, all six terms are equal. We compute just one of these six terms and “cancel out” the normalization factor. Then, using Eq. (2.44) to evaluate the integral of the first term, we obtain

$$\begin{aligned}
\left\langle \left| \psi_1 \psi_2 \psi_3 \right| \left| \sum_{i=1}^3 \hat{h}(\mathbf{r}_i) \right| \left| \psi_1 \psi_2 \psi_3 \right| \right\rangle &= \left\langle \left( \psi_1 \psi_2 \psi_3 \right) \left| \sum_{i=1}^3 \hat{h}(\mathbf{r}_i) \right| \left( \psi_1 \psi_2 \psi_3 \right) \right\rangle \\
&= \langle \psi_1 | \hat{h} | \psi_1 \rangle + \langle \psi_2 | \hat{h} | \psi_2 \rangle + \langle \psi_3 | \hat{h} | \psi_3 \rangle \\
&= \sum_{i=1}^3 \langle \psi_i | \hat{h} | \psi_i \rangle \quad (2.55)
\end{aligned}$$

The analysis is similar for arbitrary numbers of electrons. One has<sup>7</sup>

$$\begin{aligned}
& \left\langle \left| \psi_1 \psi_2 \dots \psi_N \right| \left| \sum_{i=1}^N \hat{h}(\mathbf{r}_i) \right| \left| \psi_1 \psi_2 \dots \psi_N \right| \right\rangle \\
&= \frac{1}{N!} \left\langle \left( \begin{array}{c} 1 - \sum_{i=1}^{N-1} \sum_{j=i+1}^N \mathcal{P}_{i,j} \\ \text{+ (higher-order)} \\ \text{+ (permutations)} \end{array} \right) \left| \psi_1 \dots \psi_N \right| \left| \sum_{i=1}^N \hat{h}(\mathbf{r}_i) \right| \left( \begin{array}{c} 1 - \sum_{i=1}^{N-1} \sum_{j=i+1}^N \mathcal{P}_{i,j} \\ \text{+ (higher-order)} \\ \text{+ (permutations)} \end{array} \right) \left| \psi_1 \dots \psi_N \right| \right\rangle. \quad (2.56)
\end{aligned}$$

<sup>7</sup> The general form of Eq. (2.56) is that one starts with the “reference” Hartree product, then constructs all ways of permuting two electronic coordinates, and then constructs the more complicated permutations, which consist of several sequential “exchanges” of electrons between orbitals. The “higher order” terms give Hartree-products that differ by more than two orbitals from the “reference” Hartree product, and so when the orbitals are orthogonal, they do not effect the value of 2-body operators.



- Because a permutation always changes two orbitals, all the “cross-terms” (that is, all the integrals where the Hartree product on the left-hand-side and right-hand-side are not equal) are zero.
- There are  $N!$  different permutations: there are  $N$  ways to pick orbital for the first electron,  $N-1$  ways to pick the orbital for the second electron, .... and one way to pick the orbital for the  $N^{\text{th}}$  electron.
- Because the operator,  $\sum_{i=1}^N h(\mathbf{r}_i)$ , is totally symmetric, it is invariant to permutations of the electronic coordinates. Consequently, all  $N!$  of the non-vanishing integrals have the same value.
- The final result, then, is  $N!$  times the integral of *any* of the Hartree-products occurring in the Slater determinant. For simplicity, we take the first such product and use Eq. (2.44) to evaluate the integral, obtaining

$$\begin{aligned}
\left\langle \psi_1 \psi_2 \dots \psi_N \left| \sum_{i=1}^N \hat{h}(\mathbf{r}_i) \right| \psi_1 \psi_2 \dots \psi_N \right\rangle &= \frac{1}{N!} (N!) \left\langle (\psi_1 \dots \psi_N \left| \sum_{i=1}^N \hat{h}(\mathbf{r}_i) \right| \psi_1 \dots \psi_N) \right\rangle \\
&= \sum_{i=1}^N \left\langle \psi_i \left| \hat{h} \right| \psi_i \right\rangle \prod_{\substack{j=1 \\ j \neq i}}^N \langle \psi_j | \psi_j \rangle \\
&\stackrel{\text{normalized}}{\text{orbitals}} = \sum_{i=1}^N \langle \psi_i | \hat{h} | \psi_i \rangle.
\end{aligned} \tag{2.57}$$

The normalization integral can be evaluated as a special case of Eq. (2.57). In particular, take  $\hat{h}(\mathbf{r}) = \frac{1}{N}$ . Then:

$$\begin{aligned}
\langle \psi_1 \psi_2 \dots \psi_N | 1 | \psi_1 \psi_2 \dots \psi_N \rangle &= \left\langle \psi_1 \psi_2 \dots \psi_N \left| \sum_{i=1}^N \frac{1}{N} \right| \psi_1 \psi_2 \dots \psi_N \right\rangle \\
&= \frac{1}{N!} (N!) \left\langle (\psi_1 \dots \psi_N \left| \sum_{i=1}^N \frac{1}{N} \right| \psi_1 \dots \psi_N) \right\rangle \\
&= \sum_{i=1}^N \left\langle \psi_i \left| \frac{1}{N} \right| \psi_i \right\rangle \prod_{\substack{j=1 \\ j \neq i}}^N \langle \psi_j | \psi_j \rangle \\
&= \sum_{i=1}^N \frac{1}{N} \langle \psi_i | \psi_i \rangle \prod_{\substack{j=1 \\ j \neq i}}^N \langle \psi_j | \psi_j \rangle \\
&= \left( \sum_{i=1}^N \frac{1}{N} \right) \prod_{j=1}^N \langle \psi_j | \psi_j \rangle \\
&= 1 \cdot \prod_{j=1}^N \langle \psi_j | \psi_j \rangle \\
&\stackrel{\text{normalized}}{\text{orbitals}} = 1
\end{aligned} \tag{2.58}$$

## IV. Two-Electron Integrals Between Slater Determinants

The analysis for the two-electron integrals is a bit more complicated. Again, we start with the example of a three-electron system. We have

$$\begin{aligned} & \left\langle \left| \psi_1 \psi_2 \psi_3 \right| \left| \sum_{i=1}^2 \sum_{j=i+1}^3 \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) \right| \left| \psi_1 \psi_2 \psi_3 \right| \right\rangle \\ &= \frac{1}{6} \left\langle \left( \begin{array}{c} 1 \\ -\mathcal{P}_{1,2} - \mathcal{P}_{1,3} - \mathcal{P}_{2,3} \\ +\mathcal{P}_{1,2}\mathcal{P}_{2,3} + \mathcal{P}_{1,3}\mathcal{P}_{2,3} \end{array} \right) \left| \psi_1 \psi_2 \psi_3 \right\rangle \left| \sum_{i=1}^2 \sum_{j=i+1}^3 \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) \left( \begin{array}{c} 1 \\ -\mathcal{P}_{1,2} - \mathcal{P}_{1,3} - \mathcal{P}_{2,3} \\ +\mathcal{P}_{1,2}\mathcal{P}_{2,3} + \mathcal{P}_{1,3}\mathcal{P}_{2,3} \end{array} \right) \left| \psi_1 \psi_2 \psi_3 \right\rangle \right\rangle \end{aligned} \quad (2.59)$$

We expect, as before, that because  $\sum_{i=1}^2 \sum_{j=i+1}^3 \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j)$  is invariant to permutations of the electronic coordinates, that there will be  $N! = 6$  terms that are identical.

This could be shown using methods similar to those employed for one-electron integrals, but let's use a different method. (In general, the more tools you know for doing this sort of integral, the better.) Let  $\hat{Q}(\mathbf{r}_1, \dots, \mathbf{r}_N)$  be the operator that represents any property of an electronic system. Because electrons are indistinguishable, they can be labeled in any order we choose, electronic operators cannot depend on the “order” in which we label the electrons. It follows that  $\hat{Q}(\mathbf{r}_1, \dots, \mathbf{r}_N)$  is *invariant* to permutations of the electrons. That is,

$$\hat{Q}(\dots \mathbf{r}_i \dots \mathbf{r}_j \dots) \equiv \hat{Q}(\dots \mathbf{r}_j \dots \mathbf{r}_i \dots) \quad (2.60)$$

Now let's evaluate the expectation value of  $\hat{Q}$  for a Slater determinant. For simplicity, consider the three electron case. Expanding the Slater determinant gives:<sup>8</sup>

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<sup>8</sup> If you don't understand where Eq. (2.61) comes from, evaluate the permutation operators and verify the result by comparing to the “long form” for the integral. Doing this will help you master the notation and, more importantly, the key ideas.

$$\begin{aligned}
& \left\langle \begin{pmatrix} 1 \\ -\mathcal{P}_{1,2} - \mathcal{P}_{1,3} - \mathcal{P}_{2,3} \\ +\mathcal{P}_{1,2}\mathcal{P}_{2,3} + \mathcal{P}_{1,3}\mathcal{P}_{2,3} \end{pmatrix} \middle| \psi_1 \psi_2 \psi_3 \right\rangle \hat{Q}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \begin{pmatrix} 1 \\ -\mathcal{P}_{1,2} - \mathcal{P}_{1,3} - \mathcal{P}_{2,3} \\ +\mathcal{P}_{1,2}\mathcal{P}_{2,3} + \mathcal{P}_{1,3}\mathcal{P}_{2,3} \end{pmatrix} \middle| \psi_1 \psi_2 \psi_3 \rangle \\
&= \left\langle \left( \psi_1 \psi_2 \psi_3 \middle| \hat{Q}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \right. \begin{pmatrix} 1 \\ -\mathcal{P}_{1,2} - \mathcal{P}_{1,3} - \mathcal{P}_{2,3} \\ +\mathcal{P}_{1,2}\mathcal{P}_{2,3} + \mathcal{P}_{1,3}\mathcal{P}_{2,3} \end{pmatrix} \middle| \psi_1 \psi_2 \psi_3 \right) \right\rangle \\
&+ \left\langle \left( \psi_2 \psi_1 \psi_3 \middle| \hat{Q}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \right. \begin{pmatrix} -\mathcal{P}_{1,2} \\ +1 + \mathcal{P}_{1,2}\mathcal{P}_{1,3} + \mathcal{P}_{1,2}\mathcal{P}_{2,3} \\ -\mathcal{P}_{2,3} - \mathcal{P}_{1,3} \end{pmatrix} \middle| \psi_2 \psi_1 \psi_3 \right) \right\rangle \\
&+ \left\langle \left( \psi_3 \psi_2 \psi_1 \middle| \hat{Q}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \right. \begin{pmatrix} -\mathcal{P}_{1,3} \\ +\mathcal{P}_{1,3}\mathcal{P}_{1,2} + 1 + \mathcal{P}_{1,3}\mathcal{P}_{2,3} \\ -\mathcal{P}_{2,3} - \mathcal{P}_{1,2} \end{pmatrix} \middle| \psi_3 \psi_2 \psi_1 \right) \right\rangle \\
&+ \left\langle \left( \psi_1 \psi_3 \psi_2 \middle| \hat{Q}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \right. \begin{pmatrix} -\mathcal{P}_{2,3} \\ +\mathcal{P}_{2,3}\mathcal{P}_{1,2} + \mathcal{P}_{2,3}\mathcal{P}_{1,3} + 1 \\ -\mathcal{P}_{1,2} - \mathcal{P}_{1,3} \end{pmatrix} \middle| \psi_1 \psi_3 \psi_2 \right) \right\rangle \\
&+ \left\langle \left( \psi_2 \psi_3 \psi_1 \middle| \hat{Q}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \right. \begin{pmatrix} \mathcal{P}_{1,3}\mathcal{P}_{2,3} \\ -\mathcal{P}_{2,3} - \mathcal{P}_{1,2} - \mathcal{P}_{1,3} \\ +1 + \mathcal{P}_{1,2}\mathcal{P}_{2,3} \end{pmatrix} \middle| \psi_2 \psi_3 \psi_1 \right) \right\rangle \\
&+ \left\langle \left( \psi_3 \psi_1 \psi_2 \middle| \hat{Q}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \right. \begin{pmatrix} \mathcal{P}_{1,2}\mathcal{P}_{2,3} \\ -\mathcal{P}_{1,3} - \mathcal{P}_{2,3} - \mathcal{P}_{1,2} \\ +\mathcal{P}_{1,3}\mathcal{P}_{2,3} + 1 \end{pmatrix} \middle| \psi_3 \psi_1 \psi_2 \right) \right\rangle
\end{aligned} \tag{2.61}$$

which shows that every term in the expansion has the same form—the only thing that has changed is that we have permuted the orbitals. However, because  $\hat{Q}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$  is invariant to permutation of the electronic coordinates, all six terms in Eq. (2.61) must be equal.

This general scenario occurs for any number of electrons, and we write the general result as a theorem:

**Theorem 7.1:** Let  $|\psi_1 \dots \psi_N\rangle$  be a Slater determinant and  $\hat{Q}(\mathbf{r}_1, \dots, \mathbf{r}_N)$  be an electronic operator.

Then

$$\left\langle |\psi_1 \dots \psi_N\rangle \middle| \hat{Q} \middle| |\psi_1 \dots \psi_N\rangle \right\rangle = \sqrt{N!} \left\langle \left( \psi_1 \dots \psi_N \middle| \hat{Q} \middle| \psi_1 \dots \psi_N \right) \right\rangle \tag{2.62}$$

where  $(\psi_1 \dots \psi_N)$  is the Hartree product,

$$(\psi_1 \dots \psi_N) \equiv \psi_1^*(\mathbf{z}_1) \psi_2^*(\mathbf{z}_2) \dots \psi_N^*(\mathbf{z}_N). \tag{2.63}$$

Next, note that in the derivation of the preceding theorem we never used the fact that the orbitals in the “ket” Slater determinant were identical to those in the “bra” Slater determinant. It follows that we actually have the more general (and *very* useful) theorem,

**Theorem 2:** Let  $|\psi_1 \dots \psi_N\rangle$  and  $|\psi'_1 \dots \psi'_N\rangle$  be a Slater determinants and  $\hat{Q}(\mathbf{r}_1, \dots, \mathbf{r}_N)$  be an electronic operator. Then

$$\langle \psi_1 \dots \psi_N | \hat{Q} | \psi'_1 \dots \psi'_N \rangle = \sqrt{N!} \langle \psi_1 \dots \psi_N | \hat{Q} | \psi'_1 \dots \psi'_N \rangle \quad (2.64)$$

where  $|\psi_1 \dots \psi_N\rangle$  is the Hartree product,

$$|\psi_1 \dots \psi_N\rangle \equiv \psi_1^*(\mathbf{z}_1) \psi_2^*(\mathbf{z}_2) \dots \psi_N^*(\mathbf{z}_N). \quad (2.65)$$

Returning to the two-electron case, we can use Theorem 1 to evaluate

$$\begin{aligned} & \left\langle \psi_1 \psi_2 \psi_3 \left| \sum_{i=1}^2 \sum_{j=i+1}^3 \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) \right| \psi_1 \psi_2 \psi_3 \right\rangle \\ &= \sqrt{6} \left\langle \psi_1 \psi_2 \psi_3 \left| \sum_{i=1}^2 \sum_{j=i+1}^3 \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) \right| \psi_1 \psi_2 \psi_3 \right\rangle \\ &= \frac{\sqrt{6}}{\sqrt{6}} \left\langle \psi_1 \psi_2 \psi_3 \left| \sum_{i=1}^2 \sum_{j=i+1}^3 \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) \right| \begin{pmatrix} 1 \\ -\mathcal{P}_{1,2} - \mathcal{P}_{1,3} - \mathcal{P}_{2,3} \\ +\mathcal{P}_{1,2}\mathcal{P}_{2,3} + \mathcal{P}_{1,3}\mathcal{P}_{2,3} \end{pmatrix} \psi_1 \psi_2 \psi_3 \right\rangle \\ &= \left( \left\langle \psi_1 \psi_2 \psi_3 \left| \sum_{i=1}^2 \sum_{j=i+1}^3 \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) \right| \psi_1 \psi_2 \psi_3 \right\rangle - \left\langle \psi_1 \psi_2 \psi_3 \left| \sum_{i=1}^2 \sum_{j=i+1}^3 \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) \right| \psi_2 \psi_1 \psi_3 \right\rangle \right. \\ &= \left. - \left\langle \psi_1 \psi_2 \psi_3 \left| \sum_{i=1}^2 \sum_{j=i+1}^3 \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) \right| \psi_3 \psi_2 \psi_1 \right\rangle - \left\langle \psi_1 \psi_2 \psi_3 \left| \sum_{i=1}^2 \sum_{j=i+1}^3 \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) \right| \psi_1 \psi_3 \psi_2 \right\rangle \right. \\ &= \left. + \left\langle \psi_1 \psi_2 \psi_3 \left| \sum_{i=1}^2 \sum_{j=i+1}^3 \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) \right| \psi_2 \psi_3 \psi_1 \right\rangle + \left\langle \psi_1 \psi_2 \psi_3 \left| \sum_{i=1}^2 \sum_{j=i+1}^3 \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) \right| \psi_3 \psi_1 \psi_2 \right\rangle \right) \quad (2.66) \end{aligned}$$

The first term contains two identical Hartree products, the second three terms contain Hartree products have two different orbitals, and the last two terms have Hartree-products that differ in more than two orbitals. Using the rules in the Table, then, we have that

$$\begin{aligned}
& \left\langle \left| \psi_1 \psi_2 \psi_3 \right| \left| \sum_{i=1}^2 \sum_{j=i+1}^3 \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) \right| \left| \psi_1 \psi_2 \psi_3 \right| \right\rangle \\
&= \left( \begin{aligned} & \sum_{i=1}^2 \sum_{j=i+1}^3 \langle \psi_i \psi_j | \hat{v}_{ee} | \psi_i \psi_j \rangle \\ & - \langle \psi_1 \psi_2 | \hat{v}_{ee} | \psi_2 \psi_1 \rangle - \langle \psi_1 \psi_3 | \hat{v}_{ee} | \psi_3 \psi_1 \rangle - \langle \psi_2 \psi_3 | \hat{v}_{ee} | \psi_3 \psi_2 \rangle \\ & + 0 + 0 \end{aligned} \right) \tag{2.67} \\
&= \sum_{i=1}^2 \sum_{j=i+1}^3 \langle \psi_i \psi_j | \hat{v}_{ee} | \psi_i \psi_j \rangle - \sum_{i=1}^2 \sum_{j=i+1}^3 \langle \psi_i \psi_j | \hat{v}_{ee} | \psi_j \psi_i \rangle \\
&= \sum_{i=1}^2 \sum_{j=i+1}^3 \left( \langle \psi_i \psi_j | \hat{v}_{ee} | \psi_i \psi_j \rangle - \langle \psi_i \psi_j | \hat{v}_{ee} | \psi_j \psi_i \rangle \right)
\end{aligned}$$

After understanding this derivation, we can proceed to the general case. Namely,

$$\begin{aligned}
& \left\langle \left| \psi_1 \psi_2 \dots \psi_N \right| \left| \sum_{i=1}^{N-1} \sum_{j=i+1}^N \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) \right| \left| \psi_1 \psi_2 \dots \psi_N \right| \right\rangle \\
& \stackrel{Th.1}{=} \left\langle \left( \psi_1 \psi_2 \dots \psi_N \left| \sum_{i=1}^{N-1} \sum_{j=i+1}^N \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) \right| \psi_1 \psi_2 \dots \psi_N \right) \right\rangle \\
& = \left\langle \left( \psi_1 \psi_2 \dots \psi_N \left| \sum_{i=1}^{N-1} \sum_{j=i+1}^N \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) \right| \left( 1 - \sum_{i=1}^{N-1} \sum_{j=i+1}^N \mathcal{P}_{i,j} \right) \right. \right. \\
& \quad \left. \left. + \left( \text{higher-order} \right) \right) \psi_1 \dots \psi_N \right) \right\rangle \\
& \quad \left. + \left( \text{permutations} \right) \right) \left| \psi_1 \dots \psi_N \right\rangle \\
& = \left\langle \left( \psi_1 \psi_2 \dots \psi_N \left| \sum_{i=1}^{N-1} \sum_{j=i+1}^N \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) \right| \psi_1 \dots \psi_N \right) \right\rangle \\
& \quad + \left\langle \left( \psi_1 \psi_2 \dots \psi_N \left| \sum_{A=1}^{N-1} \sum_{B=A+1}^N \hat{v}_{ee}(\mathbf{r}_A, \mathbf{r}_B) \right| \sum_{i=1}^{N-1} \sum_{j=i+1}^N \mathcal{P}_{i,j} \right) \psi_1 \dots \psi_N \right\rangle \\
& \quad + \left\langle \left( \psi_1 \psi_2 \dots \psi_N \left| \sum_{i=1}^{N-1} \sum_{j=i+1}^N \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) \right| \left( \text{higher-order} \right) \right) \psi_1 \dots \psi_N \right\rangle \\
& \quad \left( \text{permutations} \right) \\
& = \sum_{i=1}^{N-1} \sum_{j=i+1}^N \langle \psi_i \psi_j | \hat{v}_{ee} | \psi_i \psi_j \rangle \prod_{\substack{k=1 \\ k \neq i, j}}^N \langle \psi_k | \psi_k \rangle \\
& \quad - \sum_{i=1}^{N-1} \sum_{j=i+1}^N \left\langle \left( \psi_1 \psi_2 \dots \psi_N \left| \sum_{A=1}^{N-1} \sum_{B=A+1}^N \hat{v}_{ee}(\mathbf{r}_A, \mathbf{r}_B) \right| \mathcal{P}_{i,j} \right) \psi_1 \dots \psi_N \right\rangle \prod_{\substack{k=1 \\ k \neq i, j}}^N \langle \psi_k | \psi_k \rangle \\
& \quad + 0 \\
& = \sum_{i=1}^{N-1} \sum_{j=i+1}^N \langle \psi_i \psi_j | \hat{v}_{ee} | \psi_i \psi_j \rangle \prod_{\substack{k=1 \\ k \neq i, j}}^N \langle \psi_k | \psi_k \rangle - \sum_{i=1}^{N-1} \sum_{j=i+1}^N \langle \psi_i \psi_j | \hat{v}_{ee} | \psi_j \psi_i \rangle \prod_{\substack{k=1 \\ k \neq i, j}}^N \langle \psi_k | \psi_k \rangle \\
& = \sum_{i=1}^{N-1} \sum_{j=i+1}^N \left[ \left( \langle \psi_i \psi_j | \hat{v}_{ee} | \psi_i \psi_j \rangle - \langle \psi_i \psi_j | \hat{v}_{ee} | \psi_j \psi_i \rangle \right) \prod_{\substack{k=1 \\ k \neq i, j}}^N \langle \psi_k | \psi_k \rangle \right]
\end{aligned} \tag{2.68}$$

## V. The Energy of a Slater Determinant.

We now have all the tools we require to evaluate the energy of a Slater determinant. We have that,

$$\begin{aligned}
E_{sl}[\Phi] & \equiv \frac{\langle \Phi | \hat{H} | \Phi \rangle}{\langle \Phi | \Phi \rangle} \\
& = \frac{\left\langle \left| \psi_1 \dots \psi_N \right| \left| \sum_{i=1}^N h(\mathbf{r}_i) \right| \left| \psi_1 \dots \psi_N \right| \right\rangle + \left\langle \left| \psi_1 \dots \psi_N \right| \left| \sum_{i=1}^{N-1} \sum_{j=i+1}^N \hat{v}_{ee}(\mathbf{r}_i, \mathbf{r}_j) \right| \left| \psi_1 \dots \psi_N \right| \right\rangle}{\langle \psi_1 \dots \psi_N | \psi_1 \dots \psi_N \rangle}
\end{aligned} \tag{2.69}$$

and, substituting in the results from Eqs. (2.57), (2.58), and (2.68)

$$E_{Sl}[\Phi] = \frac{\left( \sum_{i=1}^N \langle \psi_i | \hat{h} | \psi_i \rangle \prod_{\substack{k=1 \\ k \neq i}}^N \langle \psi_k | \psi_k \rangle + \sum_{i=1}^{N-1} \sum_{j=i+1}^N \left[ \left( \langle \psi_i \psi_j | \hat{v}_{ee} | \psi_i \psi_j \rangle - \langle \psi_i \psi_j | \hat{v}_{ee} | \psi_j \psi_i \rangle \right) \prod_{\substack{k=1 \\ k \neq i, j}}^N \langle \psi_k | \psi_k \rangle \right] \right)}{\prod_{k=1}^N \langle \psi_k | \psi_k \rangle} \quad (2.70)$$

$$= \left( \sum_{i=1}^N \frac{\langle \psi_i | \hat{h} | \psi_i \rangle}{\langle \psi_i | \psi_i \rangle} + \sum_{i=1}^{N-1} \sum_{j=i+1}^N \left( \frac{\langle \psi_i \psi_j | \hat{v}_{ee} | \psi_i \psi_j \rangle - \langle \psi_i \psi_j | \hat{v}_{ee} | \psi_j \psi_i \rangle}{\langle \psi_i | \psi_i \rangle \langle \psi_j | \psi_j \rangle} \right) \right)$$

If the orbitals are not only orthogonal, but normalized, then we have

$$E_{Sl}[\Phi] = \sum_{i=1}^N \langle \psi_i | \hat{h} | \psi_i \rangle + \sum_{i=1}^{N-1} \sum_{j=i+1}^N \left( \langle \psi_i \psi_j | \hat{v}_{ee} | \psi_i \psi_j \rangle - \langle \psi_i \psi_j | \hat{v}_{ee} | \psi_j \psi_i \rangle \right). \quad (2.71)$$

For convenience, we introduce notation for the one-electron integrals,

$$\begin{aligned} h_i &\equiv \langle \psi_i | \hat{h} | \psi_i \rangle \\ &= \left\langle \psi_i \left| -\frac{\nabla_i^2}{2} + v(\mathbf{r}_i) \right| \psi_i \right\rangle \\ &= \int \psi_i^*(\mathbf{r}) \left( -\frac{\nabla^2}{2} + v(\mathbf{r}) \right) \psi_i(\mathbf{r}) d\mathbf{r} \end{aligned} \quad (2.72)$$

and two-electron integrals, which we name the *Coulomb integrals*,

$$\begin{aligned} J_{ij} &\equiv \langle \psi_i \psi_j | \hat{v}_{ee} | \psi_i \psi_j \rangle \\ &= \iint \frac{\psi_i^*(\mathbf{z}_i) \psi_j^*(\mathbf{z}_j) \psi_i(\mathbf{z}_i) \psi_j(\mathbf{z}_j)}{|\mathbf{r}_i - \mathbf{r}_j|} d\mathbf{z}_i d\mathbf{z}_j \end{aligned} \quad (2.73)$$

and the *exchange integrals*,

$$\begin{aligned} K_{ij} &\equiv \langle \psi_i \psi_j | \hat{v}_{ee} | \psi_j \psi_i \rangle \\ &= \iint \frac{\psi_i^*(\mathbf{z}_i) \psi_j^*(\mathbf{z}_j) \psi_j(\mathbf{z}_i) \psi_i(\mathbf{z}_j)}{|\mathbf{r}_i - \mathbf{r}_j|} d\mathbf{z}_i d\mathbf{z}_j \end{aligned} \quad (2.74)$$

The above formulae are all correct when the orbitals are real (which is the usual case), and when the orbitals are complex the only change is that the exchange integral should be replaced by

$$K_{ij} \xrightarrow{\text{complex orbitals}} \frac{K_{ij} + K_{ji}}{2}. \quad (2.75)$$

We will assume the orbitals are real in all subsequent work, but by making the change in Eq. (2.75), the following treatment is easily generalized.

It is helpful to reverse the notational change in Eq. (1.16) and show the spin coordinates of the orbitals explicitly. Denoting the spin of electron  $i$  when it is in the spin-orbital  $\psi_k(\mathbf{z})$  as  $\sigma_k(i)$ , we have

$$\begin{aligned}
J_{ij} &= \iint \frac{\psi_i^*(\mathbf{z}_i) \psi_j^*(\mathbf{z}_j) \psi_i(\mathbf{z}_i) \psi_j(\mathbf{z}_j)}{|\mathbf{r}_i - \mathbf{r}_j|} d\mathbf{z}_i d\mathbf{z}_j \\
&= \iint \frac{\psi_i^*(\mathbf{r}_i) \psi_j^*(\mathbf{r}_j) \psi_i(\mathbf{r}_i) \psi_j(\mathbf{r}_j)}{|\mathbf{r}_i - \mathbf{r}_j|} d\mathbf{r}_i d\mathbf{r}_j \cdot \langle \sigma_i(i) \sigma_j(j) | \sigma_i(i) \sigma_j(j) \rangle \\
&= \iint \frac{\psi_i^*(\mathbf{r}) \psi_j^*(\mathbf{r}') \psi_i(\mathbf{r}) \psi_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \cdot \langle \sigma_i | \sigma_i \rangle \langle \sigma_j | \sigma_j \rangle \\
&= \iint \frac{|\psi_i(\mathbf{r})|^2 |\psi_j(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'
\end{aligned} \tag{2.76}$$

which reveals that the  $J_{ij}$  is the classical Coulomb repulsion energy between two charge distributions: one due to the electron in  $\psi_i(\mathbf{r})$  one from the electron in  $\psi_j(\mathbf{r})$ . Because this is a classical electrostatic interaction, there is no dependence on the spin. In addition, we note that

$$J_{ij} = J_{ji} \tag{2.77}$$

This allows us to rewrite the sum of the Coulomb integrals,<sup>9</sup>

$$\begin{aligned}
\sum_{1 \leq i < j}^N J_{ij} &= \sum_{i=1}^{N-1} \sum_{j=i+1}^N J_{ij} \\
&= \sum_{i=1}^{N-1} \sum_{j=i+1}^N J_{ji} \\
&= \sum_{j=1}^N \sum_{i=1}^{j-1} J_{ji} \\
&= \sum_{i=2}^N \sum_{j=1}^{i-1} J_{ij} \\
&= \sum_{i > j > 1}^N J_{ij}
\end{aligned} \tag{2.78}$$

which allows us to write

$$\sum_{i=1}^{N-1} \sum_{j=i+1}^N J_{ij} = \sum_{i=2}^N \sum_{j=1}^{i-1} J_{ij} = \frac{1}{2} \sum_{i=1}^N \sum_{\substack{j=1 \\ j \neq i}}^N J_{ij}. \tag{2.79}$$

The analysis for the exchange integrals is similar. Analogous to Eq. (2.76) we have (assuming real orbitals)

<sup>9</sup> This sort of analysis is typical of the sort of “index games” we play in quantum chemistry. Here, because  $J_{ij} = J_{ji}$ , we can calculate the Coulomb energy by evaluating the Coulomb repulsion between orbital  $i$  and orbital  $j$  when  $i < j$  or, equivalently, evaluate the interactions between orbitals  $i$  and  $j$  when  $i > j$ . We can even, as we do here, take the sum of both possibilities and divide by two (since we have counted the “interaction” between the orbitals twice. Indeed, we would have obtained the “symmetric” formula if we had used the “symmetric” for the electron-electron repulsion operator, that is, used

$$\hat{V}_{ee} \equiv \frac{1}{2} \sum_{i=1}^N \sum_{\substack{j=1 \\ j \neq i}}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

instead of

$$\hat{V}_{ee} \equiv \sum_{i=1}^{N-1} \sum_{j=i+1}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}.$$



$$\begin{aligned}
K_{ij} &= \iint \frac{\psi_i(\mathbf{z}_i)\psi_j(\mathbf{z}_j)\psi_j(\mathbf{z}_i)\psi_i(\mathbf{z}_j)}{|\mathbf{r}_i - \mathbf{r}_j|} d\mathbf{z}_i d\mathbf{z}_j \\
&= \iint \frac{\psi_i(\mathbf{r}_i)\psi_j(\mathbf{r}_j)\psi_j(\mathbf{r}_i)\psi_i(\mathbf{r}_j)}{|\mathbf{r}_i - \mathbf{r}_j|} d\mathbf{r}_i d\mathbf{r}_j \cdot \langle \sigma_i(i) \sigma_j(j) | \sigma_j(i) \sigma_i(j) \rangle \\
&= \iint \frac{\psi_i(\mathbf{r})\psi_j(\mathbf{r}')\psi_j(\mathbf{r})\psi_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \cdot \langle \sigma_i | \sigma_j \rangle \langle \sigma_j | \sigma_i \rangle \\
&= \delta_{\sigma_j \sigma_i} \iint \frac{(\psi_i(\mathbf{r})\psi_j(\mathbf{r}))(\psi_j(\mathbf{r}')\psi_i(\mathbf{r}'))}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'
\end{aligned} \tag{2.80}$$

Unlike the Coulomb integral, the exchange integral does depend on the spins and, in particular, is zero unless the orbitals,  $\psi_i(\mathbf{z})$  and  $\psi_j(\mathbf{z})$ , have the same spin. Just like Eq. (2.77)

$$K_{ij} = K_{ji} \tag{2.81}$$

and, tracing through the analysis in Eq. (2.78) with  $K_{ij}$  replacing  $J_{ij}$ , we find that we can again write

$$\underbrace{\sum_{i=1}^{N-1} \sum_{j=i+1}^N K_{ij}}_{i < j \text{ form}} = \underbrace{\sum_{i=2}^N \sum_{j=1}^{i-1} K_{ij}}_{i > j \text{ form}} = \underbrace{\frac{1}{2} \sum_{i=1}^N \sum_{\substack{j=1 \\ j \neq i}}^N K_{ij}}_{i \neq j \text{ form}} \tag{2.82}$$

and if we recognize that

$$K_{ii} = J_{ii} \tag{2.83}$$

we can write the energy expression for a Slater determinant, (2.71), as

$$\begin{aligned}
E_{Sl}[\Phi] &\equiv \langle \psi_1 \dots \psi_N | \hat{H} | \psi_1 \dots \psi_N \rangle \\
&= \sum_{i=1}^N h_i + \sum_{i=1}^{N-1} \sum_{j=i+1}^N (J_{ij} - K_{ij}) \\
&= \sum_{i=1}^N h_i + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N (J_{ij} - K_{ij}) \\
&= \sum_{i=1}^N \left( h_i + \frac{1}{2} \sum_{j=1}^N (J_{ij} - K_{ij}) \right).
\end{aligned} \tag{2.84}$$

The Coulomb integrals are always positive, as is clear because the integrand is always positive. The integrand in the exchange integrals is not always positive, but the exchange integrals are still positive whenever the orbitals therein have the same spin. On a mathematical level, this is because  $\iint d\mathbf{r} d\mathbf{r}' \left[ \frac{1}{|\mathbf{r} - \mathbf{r}'|} \times \right]$  is a positive-definite integral operator (often we just say that  $\frac{1}{|\mathbf{r} - \mathbf{r}'|}$  is a positive-definite “kernel”), and so

$$\iint f(\mathbf{r}) \frac{1}{|\mathbf{r} - \mathbf{r}'|} f(\mathbf{r}') d\mathbf{r} d\mathbf{r}' > 0 \tag{2.85}$$

(provided  $f(\mathbf{r}) \neq 0$ ) for just the same reason that, for any positive definite matrix,  $P$ ,

$$\mathbf{x}^T P \mathbf{x} > 0 \tag{2.86}$$

for any non-zero vector  $\mathbf{x}$ . (There is also a proof using Poisson’s equation<sup>10</sup> and Green’s first identity.) Intuitively, the exchange integral,  $K_{ij}$ , is positive because it is the Coulomb interaction

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<sup>10</sup> Poisson’s equation indicates that for any well-behaved charge density,  $q(\mathbf{r})$ ,

energy between a charge distribution,  $\psi_i(\mathbf{r})\psi_j(\mathbf{r})$ , and itself. Rewriting the exchange integral using the substitution  $\mathbf{x} = \mathbf{r}' - \mathbf{r}$ , we have

$$K_{ij} = \delta_{\sigma_j \sigma_i} \iint \frac{(\psi_i(\mathbf{r})\psi_j(\mathbf{r}))(\psi_j(\mathbf{r}+\mathbf{x})\psi_i(\mathbf{r}+\mathbf{x}))}{|\mathbf{x}|} d\mathbf{r} d\mathbf{x} \quad (2.87)$$

For small  $x \equiv |\mathbf{x}|$ , we see that the integrand will tend to be large (the denominator is small) and positive,<sup>11</sup> since  $\psi_i(\mathbf{r})\psi_j(\mathbf{r})$  and  $\psi_i(\mathbf{r}+\mathbf{x})\psi_j(\mathbf{r}+\mathbf{x})$  will tend to have the same sign for small  $x$ . For larger interelectron distances,  $x$ , it is possible to have a favorable interaction between the charge distribution (the integrand can be negative), but this is mitigated by the fact the denominator is larger. That is, a charge distribution is most sensitive, owing to the  $\frac{1}{r}$  nature of the Coulomb force, to what is happening “nearby”, and for the interaction of a charge distribution with itself, this is always “unfavorable”, resulting in a repulsive interaction.

The magnitude of the exchange-integral is smaller than that of the associated Coulomb integral, and so

$$J_{ij} - K_{ij} > 0 \quad (2.88)$$

for all  $i$  and  $j$ . Equation (2.88) is plausible because  $J_{ij}$  represents the interaction between two distributions with unit charge (because  $\int |\psi_i(\mathbf{r})|^2 d\mathbf{r} = \int |\psi_j(\mathbf{r})|^2 d\mathbf{r} = 1$ ), while  $K_{ij}$  represents the interaction between two distributions with zero charge (because  $\int \psi_i(\mathbf{r})\psi_j(\mathbf{r}) d\mathbf{r} = 0$ ).

To prove Eq. (2.88), we start by noting that.

$$\iint \frac{|\psi_i(\mathbf{r})\psi_j(\mathbf{r}')||\psi_i(\mathbf{r}')\psi_j(\mathbf{r})|}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' > \iint \frac{\psi_i(\mathbf{r})\psi_j(\mathbf{r})\psi_i(\mathbf{r}')\psi_j(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \equiv K_{ij} \quad (2.89)$$

To derive Eq. (2.89), use the fact that  $|x| \geq x$ , with the equality holding only for non-negative numbers,  $x$ . (The inequality is strict because the spatial portions of orbitals with the same spin must be orthogonal,  $\int \psi_i(\mathbf{r})\psi_j(\mathbf{r}) d\mathbf{r} = 0$ , which implies that  $\psi_i(\mathbf{r})\psi_j(\mathbf{r}')$  will not be positive for all choices of  $\mathbf{r}$  and  $\mathbf{r}'$ .) Next, we use the Cauchy inequality,<sup>12</sup>

$$2|x||y| \leq x^2 + y^2, \quad (2.90)$$

to obtain

$$\nabla^2 \left( \int \frac{q(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' \right) = -4\pi q(\mathbf{r}).$$

<sup>11</sup> Remember that the interaction energy is positive (unfavorable/repulsive) for “like charges” and negative (favorable/attractive) for unlike charges,

<sup>12</sup> The Cauchy inequality just says that the “cross-term” in  $(x+y)^2$  is less than the sum of the “direct terms.” It is most easily proved using polar coordinates. Then

$$2xy = 2r^2 \cos(\theta) \sin(\theta) = r^2 \sin(2\theta) \leq r^2 |\sin(2\theta)| = 2|x||y| \leq r^2 = x^2 + y^2.$$

$$\begin{aligned}
2K_{ij} &< 2 \iint \frac{|\psi_i(\mathbf{r})\psi_j(\mathbf{r}')| |\psi_i(\mathbf{r}')\psi_j(\mathbf{r})|}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}' \\
&< \iint \frac{|\psi_i(\mathbf{r})\psi_j(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + \iint \frac{|\psi_i(\mathbf{r}')\psi_j(\mathbf{r})|^2}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}' \\
&< \iint \frac{|\psi_i(\mathbf{r})|^2 |\psi_j(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + \iint \frac{|\psi_i(\mathbf{r}')|^2 |\psi_j(\mathbf{r})|^2}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}' \\
&< J_{ij} + J_{ji} \\
&< 2J_{ij}.
\end{aligned} \tag{2.91}$$

For molecules composed of “light” atoms (H-Ar), the exchange integrals tend to be, on average, about an order of magnitude smaller than the Coulomb integrals.

We conclude this section by briefly discussing the Energy formula for the Slater determinant, Eq. (2.84), which we repeat for convenience.

$$\begin{aligned}
E_{Sl}[\Phi] &\equiv \langle \psi_1 \dots \psi_N | \hat{H} | \psi_1 \dots \psi_N \rangle \\
&= \sum_{i=1}^N \left( h_i + \frac{1}{2} \sum_{j=1}^N (J_{ij} - K_{ij}) \right).
\end{aligned} \tag{2.92}$$

The energy of a Slater determinant, then, consists of

- The sum of the kinetic energy and electron-nuclear attraction energies for each orbital,  $h_i$ .
- The Coulomb repulsion,  $J_{ij}$ , between each orbital,  $\psi_i(\mathbf{z})$  and every other orbital. Note that  $J_{ij} = J_{ji}$ .
- An “exchange energy” that diminishes the Coulomb repulsion between orbitals with the same spin. However, because  $K_{ij} = 0$  if the spins of orbitals  $\psi_i(\mathbf{z})$  and  $\psi_j(\mathbf{z})$ ,  $\sigma_i$  and  $\sigma_j$ , are different, there is no exchange effect when electrons have opposite spin. This provides further evidence for the fact “exchange” measures the energetic effects of the Pauli exclusion principle. In addition,  $K_{ij} < J_{ij}$  in all cases, so the Pauli exclusion principle never completely “cancels out” the Coulomb repulsion between electrons. The exchange is an energetically important effect however, lowering the energy by approximately 10 eV per electron pair (for molecules formed with atoms from the first row of the periodic table).

## VI. Digression on the Calculus of Variations

Recall that the Hartree-Fock method is obtained by finding the Slater determinant of orbitals with the lowest energy, Eq. (1.20). This requires that one be able to determine how the energy changes as the orbitals change, so that we can construct a method for revising the orbitals from an initial “guess” approximation towards the exact answer.

As motivation for the approach we shall take, consider the similar problem of minimizing a function,  $f(\mathbf{x})$ , where  $\mathbf{x} = \begin{bmatrix} x_1 & x_2 & \dots & x_d \end{bmatrix}^T$  is a  $d$ -dimensional vector. Given an initial guess for the minimizing value of  $\mathbf{x}$ , which we call  $\tilde{\mathbf{x}}$ , the minimum value of the function can be found by computing the gradient of the function at the point  $\tilde{\mathbf{x}}$ ,  $\nabla f(\tilde{\mathbf{x}})$ , and moving in the direction of decrease, changing  $\tilde{\mathbf{x}}$  to  $\tilde{\mathbf{x}} - \epsilon \nabla f(\tilde{\mathbf{x}})$  ( $\epsilon > 0$ ), until the minimum is found. Alternatively, if the

function is *convex*,<sup>13</sup> so that there is only one place where  $\nabla f(\tilde{\mathbf{x}}) = 0$ , then, instead of minimizing the function  $f(\mathbf{x})$ , we can solve for the point,  $\mathbf{x}_{\min}$ , where

$$\nabla f(\mathbf{x}_{\min}) = 0. \quad (2.93)$$

This suggests that, in order to find the optimum Slater determinant, we need a way to generalize the concept of a derivative from functions whose arguments are variables, like  $f(\mathbf{x})$ , to functions whose arguments are other functions, like the energy of a Slater determinant, (we revise (2.70) in accord with Eqs. (2.79) and (2.82)),

$$E_{Sl}[\Phi] = \left( \sum_{i=1}^N \frac{\langle \psi_i | \hat{h} | \psi_i \rangle}{\langle \psi_i | \psi_i \rangle} + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \left( \frac{\langle \psi_i \psi_j | \hat{v}_{ee} | \psi_i \psi_j \rangle - \langle \psi_i \psi_j | \hat{v}_{ee} | \psi_j \psi_i \rangle}{\langle \psi_i | \psi_i \rangle \langle \psi_j | \psi_j \rangle} \right) \right). \quad (2.94)$$

Some nomenclature: A function of a function is called a *functional*, and its argument is enclosed in brackets (instead of parentheses). When a functional is a function of both functions and variables, the arguments are traditionally separated by a semicolon, with the functions listed first. E.g.,  $F[f; \mathbf{x}]$  is a functional of  $f(\mathbf{x})$  and a function of  $\mathbf{x}$ . Often the arguments of functionals are omitted when they are clear from context, just as we often just write the wave function as  $\Psi$ , conveniently “forgetting” to write out its dependence on the spatial and spin coordinates of the electrons.

The *functional derivative* describes how a functional changes when the functions on which it depends change, just as the usual derivative describes how a function changes when the variables on which it depends change. Suppose we change the argument of a function from  $\mathbf{x}$  to  $\mathbf{x} + d\mathbf{x}$ . Then the value of the function changes according to

$$\begin{aligned} df &\equiv f(\mathbf{x} + d\mathbf{x}) - f(\mathbf{x}) \\ &= \nabla f(\mathbf{x}) \cdot d\mathbf{x} + \mathcal{O}(d\mathbf{x} \cdot d\mathbf{x}) \\ &= \sum_{i=1}^d \frac{\partial f(\mathbf{x})}{\partial x_i} dx_i + \mathcal{O}\left(\sum_{i=1}^d d(dx_i)^2\right) \end{aligned} \quad (2.95)$$

where the first line is the definition of the derivative—the derivative maps changes in  $\mathbf{x}$  to changes in  $f(\mathbf{x})$  with errors proportional to the magnitude of the change squared (for small changes). The second line uses the definition of the dot product, and the notation  $\mathcal{O}(d\mathbf{x} \cdot d\mathbf{x})$  indicates that the formula is exact, except for errors proportional to  $d\mathbf{x} \cdot d\mathbf{x}$ .

The formula for the functional derivative is similar. Changing the argument of the functional,  $Q[f]$ , from  $f(\mathbf{r})$  to  $f(\mathbf{r}) + \delta f(\mathbf{r})$  gives

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<sup>13</sup> A function is convex if, for any points  $\mathbf{x}$  and  $\mathbf{y}$  and any value  $0 \leq t \leq 1$ , then

$$tf(\mathbf{x}) + (1-t)f(\mathbf{y}) > f(t\mathbf{x} + (1-t)\mathbf{y}).$$

A convex function looks (very roughly) like a bowl, with a single minimum at the “bottom” of the bowl. This is the generalization of the criterion that the second derivative must be positive at a minimum, as is apparent from the fact the formula for the second derivative

$$\frac{d^2 f}{dx^2} = \lim_{h \rightarrow 0} \frac{f(r-h) + f(r+h) - 2f(r)}{h^2} > 0$$

has the same form as the convexity condition. (Take  $x = r - h$ ,  $y = r + h$ , and  $t = \frac{1}{2}$ .)

$$Q[f + \delta f] - Q[f] = \int \frac{\delta Q[f]}{\delta f(\mathbf{r})} \delta f(\mathbf{r}) d\mathbf{r} + \left( \begin{array}{l} \text{errors of proportional} \\ \text{to the size of } (\delta f(\mathbf{r}))^2 \end{array} \right), \quad (2.96)$$

and the functional derivative,  $\frac{\delta Q[f]}{\delta f(\mathbf{r})}$ , is defined as the function that maps changes in  $f(\mathbf{r})$  to changes in  $Q[f]$  according to Eq. (2.96), with the remaining error being proportional to the square of the size of the change in the function,  $\|\delta f(\mathbf{r})\|^2$ . The similarity between the functional derivative and the gradient is striking: just as there are multiple terms in the sum in (2.95) because it is possible to change  $\mathbf{x}$  in different “directions”, so also it is possible to change a function at many different “points”, and so we must integrate over all the possible places the function might change, as in Eq. (2.96).<sup>14</sup>

From this argument, we suspect that if we change the function at only one point in space, then we will obtain a “direct” formula for the functional derivative, just as when we change a function  $f(\mathbf{x})$ , in only one direction,  $x_i$ , we obtain a more conventional form for the usual derivative ( $\nabla f \cdot d\mathbf{x} \rightarrow \frac{df}{dx_i} dx_i$ ). To this end, consider the case where

$$\delta f(\mathbf{r}) = \varepsilon \delta(\mathbf{r} - \mathbf{x}). \quad (2.97)$$

Substituting Eq. (2.97) into Eq. (2.96), we find that

$$\begin{aligned} Q[f + \varepsilon \delta(\mathbf{r} - \mathbf{x})] - Q[f] &= \int \frac{\delta Q}{\delta f(\mathbf{r})} \varepsilon \delta(\mathbf{r} - \mathbf{x}) d\mathbf{r} + \left( \begin{array}{l} \text{errors proportional} \\ \text{to } \varepsilon^2 \end{array} \right) \\ Q[f + \varepsilon \delta(\mathbf{r} - \mathbf{x})] - Q[f] &= \varepsilon \frac{\delta Q}{\delta f(\mathbf{x})} + \left( \begin{array}{l} \text{errors proportional} \\ \text{to } \varepsilon^2 \end{array} \right) \\ \frac{Q[f + \varepsilon \delta(\mathbf{r} - \mathbf{x})] - Q[f]}{\varepsilon} &= \frac{\delta Q[f]}{\delta f(\mathbf{x})} + \left( \begin{array}{l} \text{errors} \\ \text{proportional} \\ \text{to } \varepsilon \end{array} \right) \\ \lim_{\varepsilon \rightarrow 0} \frac{Q[f(\mathbf{r}) + \varepsilon \delta(\mathbf{r} - \mathbf{x})] - Q[f]}{\varepsilon} &= \frac{\delta Q[f]}{\delta f(\mathbf{x})} + 0 \\ \left( \frac{\partial Q[f(\mathbf{r}) + \varepsilon \delta(\mathbf{r} - \mathbf{x})]}{\partial \varepsilon} \right)_{\varepsilon=0} &= \frac{\delta Q[f]}{\delta f(\mathbf{x})}. \end{aligned} \quad (2.98)$$

Equation (2.98) is a key formula,<sup>15</sup> and is very useful for evaluating functional derivatives.

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<sup>14</sup> The similarity is even more striking if you remember the Riemann sum definition of the integral, whereby we can write

$$Q[f + \delta f] - Q[f] \approx \lim_{N \rightarrow \infty} \left[ \sum_{i=0}^N \left( \frac{\delta Q[f]}{\delta f\left(a + i \frac{(b-a)}{N}\right)} \delta f\left(a + i \frac{(b-a)}{N}\right) \right) \left( \frac{(b-a)}{N} \right) \right] \equiv \int_a^b \frac{\delta Q[f]}{\delta f(x)} \delta f(x) dx$$

<sup>15</sup> The last line in Eq. (2.98) uses a somewhat non-standard definition of the derivative. It is equivalent to the usual definition. In particular, from the “usual” definition of the derivative we have

Another method for evaluating functional derivatives is to use the definition, Eq. (2.96), directly. Take the difference between  $Q[f + \delta f]$  and  $Q[f]$  and find the coefficient of  $\delta f(\mathbf{r})$  in the expression

$$Q[f + \delta f] - Q[f] = \int q(\mathbf{r}) \delta f(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \iint q^{(2)}(\mathbf{r}, \mathbf{r}') \delta f(\mathbf{r}) \delta f(\mathbf{r}') d\mathbf{r} d\mathbf{r}' + \dots \quad (2.99)$$

Then, from Eq. (2.96), we have that  $q(\mathbf{r}) = \frac{\delta Q[f]}{\delta f(\mathbf{r})}$ . Incidentally,  $q^{(2)}(\mathbf{r}, \mathbf{r}')$  is the second functional derivative,  $\frac{\delta^2 Q[f]}{\delta f(\mathbf{r}) \delta f(\mathbf{r}')} = \frac{\delta}{\delta f(\mathbf{r}')} \left( \frac{\delta Q[f]}{\delta f(\mathbf{r})} \right)$ . (In fact, Eq. (2.99) is analogous to the Taylor series for functions,

$$f(\mathbf{x} + d\mathbf{x}) - f(\mathbf{x}) = \nabla f(\mathbf{x}) \cdot d\mathbf{x} + \frac{1}{2} d\mathbf{x} \cdot (\nabla \nabla f(\mathbf{x})) \cdot d\mathbf{x} + \dots \quad (2.100)$$

Finally, there is a useful identity that I call the Gelfand-Fomin identity, which states that for a functional that can be written as an integral of a functional,  $\mathcal{F}$ , which is a simple function of  $f(x)$ ,  $\frac{df}{dx}$ ,  $\frac{d^2 f(x)}{dx^2}$ , etc.,

$$F[f] \equiv \int \mathcal{F}\left(f, \frac{df}{dx}, \frac{d^2 f}{dx^2} \dots\right) dx \quad (2.101)$$

that

$$\frac{\delta F[f]}{\delta f(x)} = \frac{d\mathcal{F}\left[f, \frac{df}{dx}, \frac{d^2 f}{dx^2}, \dots\right]}{df(x)} - \frac{d}{dx} \left( \frac{d\mathcal{F}\left[f, \frac{df}{dx}, \frac{d^2 f}{dx^2}, \dots\right]}{d\left(\frac{df}{dx}\right)} \right) + \frac{d^2}{dx^2} \left( \frac{d\mathcal{F}\left[f, \frac{df}{dx}, \frac{d^2 f}{dx^2}, \dots\right]}{d\left(\frac{d^2 f}{dx^2}\right)} \right) - \dots \quad (2.102)$$

Equation (2.102) is derived using integration by parts.

From any of these methods, it is easy to derive a number of useful results, chief among them the

- sum rule. The functional derivative of a sum is the sum of the functional derivatives,

$$\frac{\delta F[f] + G[f]}{\delta f(x)} = \frac{\delta F[f]}{\delta f(x)} + \frac{\delta G[f]}{\delta f(x)} \quad (2.103)$$

- product rule. The functional derivative of a product is given by the formula

$$\frac{\delta F[f] G[f]}{\delta f(x)} = F[f] \frac{\delta G[f]}{\delta f(x)} + G[f] \frac{\delta F[f]}{\delta f(x)} \quad (2.104)$$

- chain rules. If  $F$  is a functional of  $f$ , which is a functional of  $f(x)$ , then

$$\begin{aligned} \lim_{\varepsilon \rightarrow 0} \frac{f(x+\varepsilon h) - f(x)}{\varepsilon} &= \lim_{\varepsilon h \rightarrow 0} \frac{f(x+\varepsilon h) - f(x)}{\varepsilon} \\ &= \lim_{\varepsilon h \rightarrow 0} \frac{f(x+\varepsilon h) - f(x)}{\varepsilon} \left( \frac{h}{h} \right) \\ &= h \lim_{\varepsilon h \rightarrow 0} \frac{f(x+\varepsilon h) - f(x)}{\varepsilon h} \\ &= h \left. \frac{df(y)}{dy} \right|_{y=x}. \end{aligned}$$

and from the “special” definition we have

$$\left. \frac{df(x+\varepsilon h)}{d\varepsilon} \right|_{\varepsilon=0} = \left. \frac{df(x+\varepsilon h)}{d(x+\varepsilon h)} \frac{d(x+\varepsilon h)}{d\varepsilon} \right|_{\varepsilon=0} = \left. \frac{df(x+\varepsilon h)}{d(x+\varepsilon h)} h \right|_{\varepsilon=0} = h \left. \frac{df(y)}{dy} \right|_{y=x}.$$

$$\frac{\delta F[g(f(x))]}{\delta f(x)} = \int \frac{\delta F}{\delta g(x')} \frac{\delta g(x')}{\delta f(x)} dx' \quad (2.105)$$

- If  $F$  is a function of  $G$ , which is a functional of  $f(x)$ , then

$$\frac{\delta F[G[f]]}{\delta f(x)} = \frac{dF}{dG} \frac{\delta G[f]}{\delta f(x)} \quad (2.106)$$

- If  $F$  is a functional of  $f(y)$ , and  $y$  is a function of  $x$ , then

$$\frac{\delta F[f]}{\delta f(y(x))} = \frac{\delta F}{\delta f(y)} \frac{dy}{dx}. \quad (2.107)$$

Each of these results resembles the usual results for “normal” derivatives, as should be expected from the “normal derivative” expression for the functional derivative, Eq. (2.98). In particular, remember that the chain rule for a function depending on several variables—say, the Gibb’s free energy as a function of  $T$  and  $P$ , is

$$\frac{\partial G}{\partial V} = \frac{\partial G}{\partial T} \cdot \frac{\partial T}{\partial V} + \frac{\partial G}{\partial P} \cdot \frac{\partial P}{\partial V} \quad (2.108)$$

and, in the general case,

$$\frac{\partial G(\mathbf{x})}{\partial y} = \sum_{i=1}^d \frac{\partial G}{\partial x_i} \frac{dx_i}{dy}. \quad (2.109)$$

The sums in Eqs. (2.108) and (2.109) (which are just “dot products”) are directly analogous (if you use the Riemann sum again) to the integral in chain rule for the functional derivative, Eq. (2.105).

These concepts are most easily demonstrated using examples. For example, choosing

$$F[f] \equiv \int (f(\mathbf{x}))^k d\mathbf{x}, \quad (2.110)$$

we can use the technique based on Eq. (2.99) to obtain

$$\begin{aligned} F[f + \delta f] - F[f] &= \int (f(\mathbf{x}) + \delta f(\mathbf{x}))^k d\mathbf{x} - \int (f(\mathbf{x}))^k d\mathbf{x} \\ &= \int (f(\mathbf{x}))^k + k(f(\mathbf{x}))^{k-1} \delta f(\mathbf{x}) + \frac{k(k-1)}{2} (f(\mathbf{x}))^{k-2} (\delta f(\mathbf{x}))^2 + \dots d\mathbf{x} - \int (f(\mathbf{x}))^k d\mathbf{x} \\ &= \int k(f(\mathbf{x}))^{k-1} \delta f(\mathbf{x}) + \frac{k(k-1)}{2} (f(\mathbf{x}))^{k-2} (\delta f(\mathbf{x}))^2 + \dots d\mathbf{x}, \end{aligned} \quad (2.111)$$

where we have used the binomial theorem in the second line. It follows from Eq. (2.99) that

$$\frac{\delta \int (f(\mathbf{r}))^k d\mathbf{r}}{\delta f(\mathbf{x})} = k f(\mathbf{x}). \quad (2.112)$$

As a second example, we can take

$$G[f] \equiv \int \mathbf{E}(\mathbf{r}) \cdot \nabla f(\mathbf{r}) d\mathbf{r}. \quad (2.113)$$

We can evaluate this using any of the above methods, but the method using the “delta-function” technique in Eq. (2.98) is particularly elegant. We have that

$$\begin{aligned}
\frac{\delta G[f]}{\delta f(\mathbf{x})} &= \left( \frac{dG[f + \varepsilon \delta(\mathbf{r} - \mathbf{x})]}{d\varepsilon} \right)_{\varepsilon=0} \\
&= \frac{d}{d\varepsilon} \int \mathbf{E}(\mathbf{r}) \cdot \nabla (f(\mathbf{r}) + \varepsilon \delta(\mathbf{r} - \mathbf{x})) d\mathbf{r} \\
&= \int \frac{d}{d\varepsilon} \mathbf{E}(\mathbf{r}) \cdot (\nabla f(\mathbf{r}) + \varepsilon \nabla \delta(\mathbf{r} - \mathbf{x})) d\mathbf{r} \\
&= \int \mathbf{E}(\mathbf{r}) \cdot (0 + \nabla \delta(\mathbf{r} - \mathbf{x})) d\mathbf{r} \\
&= -\nabla \cdot \mathbf{E}(\mathbf{x})
\end{aligned} \tag{2.114}$$

where we have used the result for the derivative of the delta function,

$$\int \mathbf{E}(\mathbf{r}) \cdot \nabla \delta(\mathbf{r} - \mathbf{x}) = -\nabla E(\mathbf{x}). \tag{2.115}$$

which is the generalization of the result

$$\int f(r) \frac{d(\delta(r-x))}{dr} dr = -f'(r). \tag{2.116}$$

You will get a lot of practice using these tools in the following sections!

## VII. The Hartree-Fock Equations

We now have all the tools we need to derive the Hartree-Fock Equations. In particular, we know how the energy depends on the orbitals, Eq. (2.94), and how to compute the way the energy changes as the orbitals change using the functional derivative. Returning, then, to the definition of the Hartree-Fock energy, Eq. (1.20), we need to minimize the energy of the Slater determinant with respect to all possible choice of orthonormal orbitals. Thus,

$$\begin{aligned}
E_{HF} &= \min_{\{\psi_i\}_{i=1}^N} E_{Sl}[\Phi] \\
&= \min_{\{\psi_i\}_{i=1}^N} \left( \sum_{i=1}^N \frac{\langle \psi_i | \hat{h} | \psi_i \rangle}{\langle \psi_i | \psi_i \rangle} + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \left( \frac{\langle \psi_i \psi_j | \hat{v}_{ee} | \psi_i \psi_j \rangle - \langle \psi_i \psi_j | \hat{v}_{ee} | \psi_j \psi_i \rangle}{\langle \psi_i | \psi_i \rangle \langle \psi_j | \psi_j \rangle} \right) \right)
\end{aligned} \tag{2.117}$$

and, just as we can find the stationary points,  $\mathbf{x}_{stat}$ , and values,  $f(\mathbf{x}_{stat})$  of a function of  $d$  variables by solving the simultaneous equations,

$$\left( \frac{\partial f(\mathbf{x}_{stat})}{\partial x_\alpha} \right)_{x_j \neq \alpha} = 0 \quad 1 \leq \alpha \leq d, \tag{2.118}$$

we can find the stationary values of the energy as a functional of the  $N$ -orbitals in a Slater determinant by solving the simultaneous equations

$$\left( \frac{\delta E_{Sl} \left[ \left\{ \psi_k^{stat} \right\}_{k=1}^N \right]}{\delta \psi_\alpha(\mathbf{r})} \right)_{\psi_j \neq \alpha} = 0 \quad 1 \leq \alpha \leq N \tag{2.119}$$

subject to the constraint that the orbitals be orthogonal.<sup>16</sup> Looking at expression (2.99) for the functional derivative, we see that it is necessary not only that  $\psi_\alpha(\mathbf{z})$  be orthogonal to the other

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<sup>16</sup> By including the form with the appropriate normalization constants in the denominator, we have obviated the need to require the orbitals to be normalized—we need only require orthogonality.



orbitals in the Slater determinant,  $\{\psi_j\}_{j=1; j \neq \alpha}^N$ , but also the  $\psi_\alpha(\mathbf{z}) + \delta\psi_\alpha(\mathbf{z})$  be orthogonal to the other orbitals. To construct such a variation, let  $\{\psi_i\}_{i=1}^\infty$  denote a complete set of spin-orbitals, with the first  $N$  elements of the set chosen so that

$$\Phi_{Sl} \equiv |\psi_1 \dots \psi_N|. \quad (2.120)$$

Then we can write<sup>17</sup>

$$\delta\psi_\alpha(\mathbf{z}) \equiv \sum_{j=N+1}^{\infty} d_{j\alpha} \psi_j(\mathbf{z}). \quad (2.121)$$

Inserting Eq. (2.121) into Eq. (2.117), we have that

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<sup>17</sup> Usually it is understood that  $d_{j\alpha}$  will be zero unless  $\psi_j(\mathbf{z})$  and  $\psi_\alpha(\mathbf{z})$  have the same spin, that is, unless  $\sigma_j = \sigma_\alpha$ . This ensures that the perturbed orbital,  $\psi_\alpha(\mathbf{z}) + \delta\psi_\alpha(\mathbf{z})$ , can still be written as a simple product of a “spin” part and a “spatial” part. We need not worry about the normalization of the modified orbital because of the terms in the denominator of Eq. (2.117).

$$\begin{aligned}
& E_{Sl} \left[ \{ \psi_k \}_{k \neq \alpha}; \psi_\alpha + \delta \psi_\alpha \right] - E_{Sl} \left[ \{ \psi_k \}_{k \neq \alpha}; \psi_\alpha \right] \\
&= \left\{ \begin{aligned}
& \sum_{\substack{i=1 \\ i \neq \alpha}}^N \frac{\langle \psi_i | \hat{h} | \psi_i \rangle}{\langle \psi_i | \psi_i \rangle} + \frac{\langle \psi_\alpha + \delta \psi_\alpha | \hat{h} | \psi_\alpha + \delta \psi_\alpha \rangle}{\langle \psi_\alpha + \delta \psi_\alpha | \psi_\alpha + \delta \psi_\alpha \rangle} \\
& + \frac{1}{2} \sum_{i=1}^N \sum_{\substack{j=1 \\ j \neq \alpha}}^N \left( \frac{\langle \psi_i \psi_j | \hat{v}_{ee} | \psi_i \psi_j \rangle - \langle \psi_i \psi_j | \hat{v}_{ee} | \psi_j \psi_i \rangle}{\langle \psi_i | \psi_i \rangle \langle \psi_j | \psi_j \rangle} \right) \\
& + \frac{1}{2} \sum_{i=1}^N \left( \frac{\langle \psi_i (\psi_\alpha + \delta \psi_\alpha) | \hat{v}_{ee} | \psi_i (\psi_\alpha + \delta \psi_\alpha) \rangle - \langle \psi_i (\psi_\alpha + \delta \psi_\alpha) | \hat{v}_{ee} | (\psi_\alpha + \delta \psi_\alpha) \psi_i \rangle}{\langle \psi_i | \psi_i \rangle \langle \psi_\alpha + \delta \psi_\alpha | \psi_\alpha + \delta \psi_\alpha \rangle} \right) \\
& + \frac{1}{2} \sum_{\substack{i=1 \\ i \neq \alpha}}^N \sum_{j=1}^N \left( \frac{\langle \psi_i \psi_j | \hat{v}_{ee} | \psi_i \psi_j \rangle - \langle \psi_i \psi_j | \hat{v}_{ee} | \psi_j \psi_i \rangle}{\langle \psi_i | \psi_i \rangle \langle \psi_j | \psi_j \rangle} \right) \\
& + \frac{1}{2} \sum_{j=1}^N \left( \frac{\langle (\psi_\alpha + \delta \psi_\alpha) \psi_j | \hat{v}_{ee} | (\psi_\alpha + \delta \psi_\alpha) \psi_j \rangle - \langle (\psi_\alpha + \delta \psi_\alpha) \psi_j | \hat{v}_{ee} | \psi_j (\psi_\alpha + \delta \psi_\alpha) \rangle}{\langle \psi_\alpha + \delta \psi_\alpha | \psi_\alpha + \delta \psi_\alpha \rangle \langle \psi_j | \psi_j \rangle} \right) \\
& + \frac{1}{2} \left( \frac{\langle (\psi_\alpha + \delta \psi_\alpha) (\psi_\alpha + \delta \psi_\alpha) | \hat{v}_{ee} | (\psi_\alpha + \delta \psi_\alpha) (\psi_\alpha + \delta \psi_\alpha) \rangle}{\langle \psi_\alpha + \delta \psi_\alpha | \psi_\alpha + \delta \psi_\alpha \rangle \langle \psi_\alpha + \delta \psi_\alpha | \psi_\alpha + \delta \psi_\alpha \rangle} \right. \\
& \quad \left. - \frac{\langle (\psi_\alpha + \delta \psi_\alpha) (\psi_\alpha + \delta \psi_\alpha) | \hat{v}_{ee} | (\psi_\alpha + \delta \psi_\alpha) (\psi_\alpha + \delta \psi_\alpha) \rangle}{\langle \psi_\alpha + \delta \psi_\alpha | \psi_\alpha + \delta \psi_\alpha \rangle \langle \psi_\alpha + \delta \psi_\alpha | \psi_\alpha + \delta \psi_\alpha \rangle} \right)
\end{aligned} \right\} \begin{aligned}
& \text{1 el.} \\
& \text{term} \\
& j \neq \alpha \\
& \text{term} \\
& j = \alpha \\
& \text{term} \\
& i \neq \alpha \\
& \text{term} \\
& i = \alpha \\
& \text{term} \\
& i = \alpha, \\
& j = \alpha \\
& \text{term}
\end{aligned} \quad (2.122)
\end{aligned}$$

$$- \left( \sum_{i=1}^N \frac{\langle \psi_i | \hat{h} | \psi_i \rangle}{\langle \psi_i | \psi_i \rangle} + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \left( \frac{\langle \psi_i \psi_j | \hat{v}_{ee} | \psi_i \psi_j \rangle - \langle \psi_i \psi_j | \hat{v}_{ee} | \psi_j \psi_i \rangle}{\langle \psi_i | \psi_i \rangle \langle \psi_j | \psi_j \rangle} \right) \right)$$

Simplifying, we have

$$\begin{aligned}
& E_{Sl} \left[ \{\psi_k\}_{k \neq \alpha}; \psi_\alpha + \delta\psi_\alpha \right] - E_{Sl} \left[ \{\psi_k\}_{k \neq \alpha}; \psi_\alpha \right] \\
&= \frac{\langle \psi_\alpha + \delta\psi_\alpha | \hat{h} | \psi_\alpha + \delta\psi_\alpha \rangle}{\langle \psi_\alpha + \delta\psi_\alpha | \psi_\alpha + \delta\psi_\alpha \rangle} - \frac{\langle \psi_\alpha | \hat{h} | \psi_\alpha \rangle}{\langle \psi_\alpha | \psi_\alpha \rangle} \\
&+ \frac{1}{2} \sum_{i=1}^N \left( \frac{\langle \psi_i (\psi_\alpha + \delta\psi_\alpha) | \hat{v}_{ee} | \psi_i (\psi_\alpha + \delta\psi_\alpha) \rangle - \langle \psi_i (\psi_\alpha + \delta\psi_\alpha) | \hat{v}_{ee} | (\psi_\alpha + \delta\psi_\alpha) \psi_i \rangle}{\langle \psi_i | \psi_i \rangle \langle \psi_\alpha + \delta\psi_\alpha | \psi_\alpha + \delta\psi_\alpha \rangle} \right. \\
&\quad \left. - \frac{\langle \psi_i \psi_\alpha | \hat{v}_{ee} | \psi_i \psi_\alpha \rangle - \langle \psi_i \psi_\alpha | \hat{v}_{ee} | \psi_\alpha \psi_i \rangle}{\langle \psi_i | \psi_i \rangle \langle \psi_\alpha | \psi_\alpha \rangle} \right) \\
&+ \frac{1}{2} \sum_{j=1}^N \left( \frac{\langle (\psi_\alpha + \delta\psi_\alpha) \psi_j | \hat{v}_{ee} | (\psi_\alpha + \delta\psi_\alpha) \psi_j \rangle - \langle (\psi_\alpha + \delta\psi_\alpha) \psi_j | \hat{v}_{ee} | \psi_j (\psi_\alpha + \delta\psi_\alpha) \rangle}{\langle \psi_\alpha + \delta\psi_\alpha | \psi_\alpha + \delta\psi_\alpha \rangle \langle \psi_j | \psi_j \rangle} \right. \\
&\quad \left. - \frac{\langle \psi_\alpha \psi_j | \hat{v}_{ee} | \psi_\alpha \psi_j \rangle - \langle \psi_\alpha \psi_j | \hat{v}_{ee} | \psi_j \psi_\alpha \rangle}{\langle \psi_\alpha | \psi_\alpha \rangle \langle \psi_j | \psi_j \rangle} \right)
\end{aligned} \tag{2.123}$$

where we have used the fact that the  $i = j = \alpha$  term is identically zero. In Eq. (2.123), the electron-electron repulsion terms on the second and third lines are identical,<sup>18</sup> and so

$$\begin{aligned}
& E_{Sl} \left[ \{\psi_k\}_{k \neq \alpha}; \psi_\alpha + \delta\psi_\alpha \right] - E_{Sl} \left[ \{\psi_k\}_{k \neq \alpha}; \psi_\alpha \right] \\
&= \frac{\langle \psi_\alpha + \delta\psi_\alpha | \hat{h} | \psi_\alpha + \delta\psi_\alpha \rangle}{\langle \psi_\alpha + \delta\psi_\alpha | \psi_\alpha + \delta\psi_\alpha \rangle} - \frac{\langle \psi_\alpha | \hat{h} | \psi_\alpha \rangle}{\langle \psi_\alpha | \psi_\alpha \rangle} \\
&+ \sum_{i=1}^N \left( \frac{\langle \psi_i (\psi_\alpha + \delta\psi_\alpha) | \hat{v}_{ee} | \psi_i (\psi_\alpha + \delta\psi_\alpha) \rangle - \langle \psi_i (\psi_\alpha + \delta\psi_\alpha) | \hat{v}_{ee} | (\psi_\alpha + \delta\psi_\alpha) \psi_i \rangle}{\langle \psi_i | \psi_i \rangle \langle \psi_\alpha + \delta\psi_\alpha | \psi_\alpha + \delta\psi_\alpha \rangle} \right. \\
&\quad \left. - \frac{\langle \psi_i \psi_\alpha | \hat{v}_{ee} | \psi_i \psi_\alpha \rangle - \langle \psi_i \psi_\alpha | \hat{v}_{ee} | \psi_\alpha \psi_i \rangle}{\langle \psi_i | \psi_i \rangle \langle \psi_\alpha | \psi_\alpha \rangle} \right) \\
&= \frac{\langle \psi_\alpha | \hat{h} | \psi_\alpha \rangle + \langle \delta\psi_\alpha | \hat{h} | \psi_\alpha \rangle + \langle \psi_\alpha | \hat{h} | \delta\psi_\alpha \rangle + \langle \delta\psi_\alpha | \hat{h} | \delta\psi_\alpha \rangle}{\langle \psi_\alpha | \psi_\alpha \rangle + \langle \delta\psi_\alpha | \psi_\alpha \rangle + \langle \psi_\alpha | \delta\psi_\alpha \rangle + \langle \delta\psi_\alpha | \delta\psi_\alpha \rangle} - \frac{\langle \psi_\alpha | \hat{h} | \psi_\alpha \rangle}{\langle \psi_\alpha | \psi_\alpha \rangle} \\
&+ \sum_{i=1}^N \left( \frac{\langle \psi_i \psi_\alpha | \hat{v}_{ee} | \psi_i \psi_\alpha \rangle + \langle \psi_i \psi_\alpha | \hat{v}_{ee} | \psi_i (\delta\psi_\alpha) \rangle + \langle \psi_i (\delta\psi_\alpha) | \hat{v}_{ee} | \psi_i \psi_\alpha \rangle + \langle \psi_i (\delta\psi_\alpha) | \hat{v}_{ee} | \psi_i (\delta\psi_\alpha) \rangle}{\langle \psi_i | \psi_i \rangle (\langle \psi_\alpha | \psi_\alpha \rangle + \langle \delta\psi_\alpha | \psi_\alpha \rangle + \langle \psi_\alpha | \delta\psi_\alpha \rangle + \langle \delta\psi_\alpha | \delta\psi_\alpha \rangle)} \right. \\
&\quad \left. - \frac{\langle \psi_i \psi_\alpha | \hat{v}_{ee} | \psi_\alpha \psi_i \rangle - \langle \psi_i \psi_\alpha | \hat{v}_{ee} | \psi_\alpha \psi_i \rangle}{\langle \psi_i | \psi_i \rangle \langle \psi_\alpha | \psi_\alpha \rangle} \right)
\end{aligned} \tag{2.124}$$

Because the operators in Eq. (2.124) are Hermitian and the orbitals are chosen to be real, we have, for example that,

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<sup>18</sup> This is true for real orbitals. Otherwise the treatment must be revised to accommodate the substitution in Eq. (2.75), with similar results.

$$\left\langle \psi_\alpha \left| \hat{h} \right| \delta \psi_\alpha \right\rangle \overset{\text{Hermitian operators}}{=} \left\langle \hat{h} \psi_\alpha \left| \delta \psi_\alpha \right\rangle = \left\langle \delta \psi_\alpha \left| \hat{h} \right| \psi_\alpha \right\rangle \overset{\text{real orbitals}}{=} \left\langle \delta \psi_\alpha \left| \hat{h} \right| \psi_\alpha \right\rangle. \quad (2.125)$$

Thus, Eq. (2.124) simplifies to

$$\begin{aligned} & E_{Sl} \left[ \{ \psi_k \}_{k \neq \alpha}; \psi_\alpha + \delta \psi_\alpha \right] - E_{Sl} \left[ \{ \psi_k \}_{k \neq \alpha}; \psi_\alpha \right] \\ &= \frac{\left\langle \psi_\alpha \left| \hat{h} \right| \psi_\alpha \right\rangle + 2 \left\langle \delta \psi_\alpha \left| \hat{h} \right| \psi_\alpha \right\rangle + \left\langle \delta \psi_\alpha \left| \hat{h} \right| \delta \psi_\alpha \right\rangle}{\left\langle \psi_\alpha \left| \psi_\alpha \right\rangle + 2 \left\langle \delta \psi_\alpha \left| \psi_\alpha \right\rangle + \left\langle \delta \psi_\alpha \left| \delta \psi_\alpha \right\rangle\right\}} - \frac{\left\langle \psi_\alpha \left| \hat{h} \right| \psi_\alpha \right\rangle}{\left\langle \psi_\alpha \left| \psi_\alpha \right\rangle} \\ &+ \sum_{i=1}^N \left[ \frac{\left\langle \psi_i \psi_\alpha \left| \hat{v}_{ee} \right| \psi_i \psi_\alpha \right\rangle + 2 \left\langle \psi_i \psi_\alpha \left| \hat{v}_{ee} \right| \psi_i (\delta \psi_\alpha) \right\rangle + \left\langle \psi_i (\delta \psi_\alpha) \left| \hat{v}_{ee} \right| \psi_i (\delta \psi_\alpha) \right\rangle}{\left\langle \psi_i \left| \psi_i \right\rangle \left( \left\langle \psi_\alpha \left| \psi_\alpha \right\rangle + 2 \left\langle \delta \psi_\alpha \left| \psi_\alpha \right\rangle + \left\langle \delta \psi_\alpha \left| \delta \psi_\alpha \right\rangle \right) \right)} \right. \\ &\quad \left. - \frac{\left\langle \psi_i \psi_\alpha \left| \hat{v}_{ee} \right| \psi_\alpha \psi_i \right\rangle - 2 \left\langle \psi_i \psi_\alpha \left| \hat{v}_{ee} \right| (\delta \psi_\alpha) \psi_i \right\rangle - \left\langle \psi_i (\delta \psi_\alpha) \left| \hat{v}_{ee} \right| (\delta \psi_\alpha) \psi_i \right\rangle}{\left\langle \psi_i \left| \psi_i \right\rangle \left\langle \psi_\alpha \left| \psi_\alpha \right\rangle} \right. \\ &\quad \left. - \frac{\left\langle \psi_i \psi_\alpha \left| \hat{v}_{ee} \right| \psi_i \psi_\alpha \right\rangle - \left\langle \psi_i \psi_\alpha \left| \hat{v}_{ee} \right| \psi_\alpha \psi_i \right\rangle}{\left\langle \psi_i \left| \psi_i \right\rangle \left\langle \psi_\alpha \left| \psi_\alpha \right\rangle} \right]. \end{aligned} \quad (2.126)$$

Remember that the orbitals in the Slater determinant,  $\{ \psi_i(\mathbf{z}) \}_{i=1}^N$ , can be chosen to be normalized. By contrast, no such assurance can be made for  $\psi_\alpha(\mathbf{z}) + \delta \psi_\alpha(\mathbf{z})$ , which may or may not be normalized. Choosing the orbitals to be normalized and using the  $n = -1$  case of the binomial theorem,

$$(1+x)^n = 1 + n \cdot x + \frac{n(n-1)}{2} x^2 + \dots \quad (2.127)$$

gives

$$(2.128)$$

Referring to Eq. (2.99), we find that for variations that preserve the orthogonality of the orbitals, we have

$$\begin{aligned} & \left( \frac{\delta E_{Sl} \left[ \{ \psi_k^{stat} \}_{k=1}^N \right]}{\delta \psi_\alpha(\mathbf{z})} \right)_{\psi_{j \neq \alpha}} = 2 \hat{h}(\mathbf{r}) \psi_\alpha(\mathbf{z}) - 2 \left\langle \psi_\alpha \left| \hat{h} \right| \psi_\alpha \right\rangle \psi_\alpha(\mathbf{z}) \\ &+ 2 \sum_{i=1}^N \left( \int \frac{\psi_i^*(\mathbf{z}') \psi_i(\mathbf{z}')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}' \psi_\alpha^*(\mathbf{z}) - \int \frac{\psi_i(\mathbf{z}') \psi_\alpha^*(\mathbf{z}')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{z}' \psi_i^*(\mathbf{z}) \right) \psi_\alpha(\mathbf{z}) \\ &- 2 \left( \sum_{i=1}^N \left\langle \psi_i \psi_\alpha \left| \hat{v}_{ee} \right| \psi_i \psi_\alpha \right\rangle - \left\langle \psi_i \psi_\alpha \left| \hat{v}_{ee} \right| \psi_\alpha \psi_i \right\rangle \right) \psi_\alpha(\mathbf{z}) \end{aligned} \quad (2.129)$$

Using the notation for the one-electron and two-electron integrals, cf. Eqs. (2.72)-(2.74), we have

$$\begin{aligned} & \left( \frac{\delta E_{Sl} \left[ \{ \psi_k^{stat} \}_{k=1}^N \right]}{\delta \psi_\alpha(\mathbf{z})} \right)_{\psi_{j \neq \alpha}} = 2 \hat{h}(\mathbf{r}) \psi_\alpha(\mathbf{z}) - 2 h_\alpha \psi_\alpha(\mathbf{z}) - 2 \left( \sum_{i=1}^N J_{\alpha i} - K_{\alpha i} \right) \psi_\alpha(\mathbf{z}) \\ &+ 2 \sum_{i=1}^N \left( \int \frac{\psi_i^*(\mathbf{z}') \psi_i(\mathbf{z}')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}' \psi_\alpha^*(\mathbf{z}) - \int \frac{\psi_i(\mathbf{z}') \psi_\alpha^*(\mathbf{z}')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{z}' \psi_i^*(\mathbf{z}) \right) \psi_\alpha(\mathbf{z}) \end{aligned} \quad (2.130)$$

In order for the energy to be stationary with respect to orthogonalization-preserving changes in the  $\alpha^{th}$  orbital, it is necessary that the functional derivative be zero. Then, from Eq. (2.130), we obtain the equation

$$\left[ \hat{h}(\mathbf{r}) + \sum_{i=1}^N \left( \int \frac{\psi_i^*(\mathbf{z}') \psi_i(\mathbf{z}')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}' \psi_\alpha^*(\mathbf{z}) - \int \frac{\psi_i(\mathbf{z}') \psi_\alpha^*(\mathbf{z}')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{z}' \psi_i^*(\mathbf{z}) \right) \right] \psi_\alpha(\mathbf{z})$$

$$= \left( h_\alpha + \sum_{i=1}^N (J_{ai} - K_{ai}) \right) \psi_\alpha(\mathbf{z}) \quad (2.131)$$

which is immediately recognized as a one-electron Schrödinger equation with potential

$$v(\mathbf{r}) + j(\mathbf{r}) - \hat{k}(\mathbf{r}) \quad (2.132)$$

and energy eigenvalue

$$\varepsilon_\alpha = h_\alpha + \sum_{i=1}^N (J_{ai} - K_{ai}), \quad (2.133)$$

where we have defined the Coulomb potential operator as

$$j(\mathbf{r}) \equiv \sum_{i=1}^N \int \frac{\psi_i^*(\mathbf{z}') \psi_i(\mathbf{z}')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}'$$

$$= \int \frac{\sum_{i=1}^N \psi_i^*(\mathbf{z}') \psi_i(\mathbf{z}')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}' \quad (2.134)$$

and the exchange potential operator as

$$\hat{k}(\mathbf{r}) \psi_\alpha(\mathbf{z}) \equiv \sum_{i=1}^N \int \frac{\psi_i^*(\mathbf{z}') \psi_\alpha(\mathbf{z}')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{z}' \psi_i(\mathbf{z})$$

$$= \int \frac{\sum_{i=1}^N \psi_i^*(\mathbf{z}') \psi_i(\mathbf{z}) \psi_\alpha(\mathbf{z}')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{z}' \quad (2.135)$$

$$= \sum_{i=1}^N \delta_{\sigma_i \sigma_\alpha} \int \frac{\psi_i^*(\mathbf{r}') \psi_\alpha(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}' \cdot \psi_i(\mathbf{z})$$

where, in analogy to expression (2.80) for the exchange energy, we have explicitly noted that there is no contribution to the exchange potential from orbitals,  $i$ , with spin,  $\sigma_i$ , that is different from the spin of the orbital being operated on,  $\sigma_\alpha$ .

With this notation, we can write the Hartree-Fock equations as the eigenvalue problem,

$$\left[ \hat{h}(\mathbf{r}) + j[\{\psi_i\}_{i=1}^N; \mathbf{r}] - \hat{k}[\{\psi_i\}_{i=1}^N; \mathbf{z}] \right] \psi_\alpha(\mathbf{z}) \equiv \varepsilon_\alpha \psi_\alpha(\mathbf{z}) \quad 1 \leq \alpha < \infty \quad (2.136)$$

or, if we write out the operator  $\hat{h}(\mathbf{r})$  in its explicit form,

$$\left[ -\frac{\nabla^2}{2} + v(\mathbf{r}) + j[\{\psi_i\}_{i=1}^N; \mathbf{r}] - \hat{k}[\{\psi_i\}_{i=1}^N; \mathbf{z}] \right] \psi_\alpha(\mathbf{z}) \equiv \varepsilon_\alpha \psi_\alpha(\mathbf{z}) \quad 1 \leq \alpha < \infty \quad (2.137)$$

Note, in particular, that both the Coulomb and the exchange operators depend on all the orbitals in the Slater determinant, and not just the orbital under question,  $\psi_\alpha(\mathbf{z})$ . Note that

$$\varepsilon_\alpha = \left\langle \psi_\alpha \left| \hat{h}(\mathbf{r}) + j[\{\psi_i\}_{i=1}^N; \mathbf{r}] - \hat{k}[\{\psi_i\}_{i=1}^N; \mathbf{z}] \right| \psi_\alpha \right\rangle \quad (2.138)$$

The entire one-electron Hamiltonian in Eq. (2.137) is often called the *one-electron Fock operator*, and denoted

$$\hat{f}[\{\psi_i\}; \mathbf{r}] \equiv \hat{h}(\mathbf{r}) + j[\{\psi_i\}; \mathbf{r}] - \hat{k}[\{\psi_i\}; \mathbf{r}]. \quad (2.139)$$

### 3. Discussion of the Hartree-Fock Equations

#### I. Solving the Hartree-Fock Equations

We summarize the results of the preceding derivation. Given a set of orthogonal and normalized spin-orbitals that form a complete set,  $\{\psi_i\}_{i=1}^{\infty}$ , we label the orbitals that are included in the Slater determinant of interest,  $\Phi_{Sl} \equiv |\psi_1 \dots \psi_N|$  as the occupied orbitals. The other orbitals we refer to as *unoccupied* or *virtual* orbitals—virtual because an orbital represents the state of an electron, and so an unoccupied state is, indeed, not a real state of an electron, but only a “virtual” one. So that we can describe the stationary states—both the ground and excited states—of the system using Slater determinants, we force the energy to be stationary with respect to the variation of the occupied orbitals; this gave us the Hartree-Fock equations,

$$\begin{aligned} \left\{ -\frac{\nabla^2}{2} + v(\mathbf{r}) + j \left[ \{\psi_i\}_{i=1}^N; \mathbf{r} \right] - \hat{k} \left[ \{\psi_i\}_{i=1}^N; \mathbf{z} \right] \right\} \psi_{\alpha}(\mathbf{z}) &\equiv \varepsilon_{\alpha} \psi_{\alpha}(\mathbf{z}) \\ \hat{f} \left[ \{\psi_i\}_{i=1}^N; \mathbf{z} \right] \psi_{\alpha}(\mathbf{z}) &= \varepsilon_{\alpha} \psi_{\alpha}(\mathbf{z}) \end{aligned} \quad (3.1)$$

where  $\hat{f}$  denoted the Fock operator. Note that all of the key contributions to the energy of an electronic system are represented: the kinetic energy of the electron, the nuclear-electron attraction, the Coulomb repulsion between orbitals, and the favorable “exchange” effects for same-spin electrons endowed by virtue of the Pauli exclusion principle. Note that there is no detailed dependence on the distance between the electrons: the repulsion potential felt by an electron in the  $\alpha^{th}$  orbital due to an electron in the  $\beta^{th}$  orbital,  $\frac{1}{|\mathbf{r}-\mathbf{r}'|}$ , has been replaced by its average value,

$\int \frac{|\psi_{\beta}(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}'$ . For this reason, Hartree-Fock theory is said to be a *mean-field theory*. (A similar mean-field theory is used to derive the van der Waal’s equation of state for an imperfect gas.) Because electrons in a Slater determinant are uncorrelated, they can be considered to move independently. Hartree-Fock theory, then, is also an example of an *independent-particle model*.

Compared to the full Schrödinger equation for a many-electron system, the Hartree-Fock equations look very simple indeed. In fact, the Hartree-Fock equations look very similar to the Schrödinger equation for a one-electron system, which is the advantage we glean from using a very simple approximate wavefunction—the Slater determinant—to model our system. However, solving the Hartree-Fock equations for the occupied (and, if desired, the unoccupied) orbitals is more difficult than finding the eigenvalues and eigenvectors of a one-electron system because the Hamiltonian for the  $\alpha^{th}$  orbital depends on the values of the other orbitals in the system,  $\psi_{i \neq \alpha}(\mathbf{r})$ , through the Coulomb and exchange potentials.

How does one solve an eigenvalue problem like the Hartree-Fock equations,

$$\hat{f} \left[ \{\psi\}; \mathbf{r} \right] \psi_{\alpha}(\mathbf{z}) = \varepsilon_{\alpha} \psi_{\alpha}(\mathbf{z})? \quad (3.2)$$

You may recall a similar situation (van der Waal’s equations; fixed point iteration). The usual method is to

1. “Guess” an initial Slater determinant of orbitals,  $\Phi^{(in)} \equiv |\psi_1^{(in)} \dots \psi_N^{(in)}|$ .
2. Construct the Coulomb,  $j \left[ \{\psi^{(in)}\}; \mathbf{r} \right]$ , and exchange,  $\hat{k} \left[ \{\psi^{(in)}\}; \mathbf{z} \right]$ , potentials using the orbitals from this Slater determinant.

3. Construct the Fock operator, Eq. (2.139). Now the Hartree-Fock equations are just a series of one-electron eigenvalue problems, Eq. (3.1), and we can solve them. One obtains a new set of orbitals,  $\{\psi_i^{(out)}\}$ , since

$$\hat{f}\left[\{\psi^{(in)}\}; \mathbf{r}\right] \psi_\alpha^{(out)}(\mathbf{z}) = \varepsilon_\alpha^{(out)} \psi_\alpha^{(out)}(\mathbf{z}) \quad (3.3)$$

4. There are two possibilities.

- It could be that the “new” orbitals and the “old” orbitals are the same—or at least similar enough that we can consider the problem to be “solved.” That is, if

$$\psi_\alpha^{(in)}(\mathbf{z}) \approx \psi_\alpha^{(out)}(\mathbf{z}) \quad (3.4)$$

for all  $\alpha$ , then substitution of Eq. (3.4) into Eq. (3.3) implies that

$$\hat{f}\left[\{\psi^{(out)}\}; \mathbf{r}\right] \psi_\alpha^{(out)}(\mathbf{z}) \approx \varepsilon_\alpha^{(out)} \psi_\alpha^{(out)}(\mathbf{z}) \quad (3.5)$$

(or, if you prefer,  $\hat{f}\left[\{\psi^{(in)}\}; \mathbf{r}\right] \psi_\alpha^{(in)}(\mathbf{z}) \approx \varepsilon_\alpha^{(in)} \psi_\alpha^{(in)}(\mathbf{z})$ ). But this implies that we actually have solved the Hartree-Fock equations, Eq. (3.2), to the desired accuracy.

- The second possibility is that the difference between the “output” orbitals,  $\{\psi_i^{(out)}\}$ , and the “input” orbitals,  $\{\psi_i^{(in)}\}$ , is unacceptably large. In this case, we know that the Hartree-Fock equations are not solved by the “input” orbitals, and we should try to improve the orbitals in some way. The simplest method—not a very good method at all—is to simply take the “output” orbitals and use them the revised “guess” for the “input” orbitals,

$$\psi_i^{(in)}(\mathbf{z}) \leftarrow \psi_i^{(out)}(\mathbf{z}). \quad (3.6)$$

then one goes back to step 2, and repeats the process until eventually the “input” and “output” orbitals are “close enough” for our purposes.

When the process converges, we say that the orbitals,  $\{\psi_i^{(out)}\}$  and the potential,  $v(\mathbf{r}) + j\left[\{\psi^{(in)}\}; \mathbf{r}\right] + \hat{k}\left[\{\psi^{(in)}\}; \mathbf{z}\right]$  are “self-consistent” or non-contradictory. Recalling that the electric field is simply the negative gradient of the potential, Hartree-Fock is thus said to be a *self-consistent field* (SCF) method: *at convergence, the field induced by the orbitals,  $-\nabla\left(v(\mathbf{r}) + j\left[\{\psi^{(in)}\}; \mathbf{r}\right] + \hat{k}\left[\{\psi^{(in)}\}; \mathbf{z}\right]\right)$  and the orbitals induced by the field through Eq. (3.3), are one and the same or, to use the technical term, consistent.*

Once the Hartree-Fock equations have been solved, we can construct the Hartree-Fock wave function by forming a determinant of the occupied Hartree-Fock orbitals,  $\Phi_{HF} \equiv \left| \psi_1^{(HF)} \dots \psi_N^{(HF)} \right|$ . The energy of this Slater determinant is given by Eq. (2.92), which we repeat here for convenience.

$$E_{HF}[\Phi_{HF}] \equiv \sum_{i=1}^N \left( h_i + \frac{1}{2} \sum_{j=1}^N (J_{ij} - K_{ij}) \right). \quad (3.7)$$

(Because they are eigenfunctions of a one-electron Hamiltonian, Eq. (3.2), we always choose the Hartree-Fock orbitals to be orthogonal and normalized.)

## II. Interpreting the Hartree-Fock Orbitals and Orbital Energies

Two of the most useful concepts in chemistry are the concept of orbitals and their energies. We may rightly ask, then: What do the Hartree-Fock orbitals and orbital energies mean? We address this question here, dispelling some prevalent myths as we go along.

### A. The total energy is not the sum of the orbitals' energies

If you put  $N$ -electrons in  $N$ -orbitals to model a system, you might suspect that the energy of the system is just the sum of all the orbital energies. This is true for some *very* primitive models, but not in Hartree-Fock theory. Comparing the energy formula, Eq. (3.7), with the expression for the sum of orbital energies obtained from the definition, Eq. (2.133),

$$\sum_{i=1}^N \varepsilon_i \equiv \sum_{i=1}^N \left( h_i + \sum_{j=1}^N (J_{ij} - K_{ij}) \right). \quad (3.8)$$

we see that

$$E_{\text{HF}} = \sum_{i=1}^N \varepsilon_i - \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N (J_{ij} - K_{ij}). \quad (3.9)$$

The reason is because there is a “double counting” of electron-electron repulsions in Eq. (3.8): the energy of an orbital is the kinetic energy plus electron-nuclear attraction energy plus the electron-electron repulsion (with exchange corrections) to all the other orbitals in the system. However, *in the total energy formula, we count the electron repulsion between orbitals  $i$  and  $j$  only once—not once for  $\psi_i(\mathbf{r})$  interacting with  $\psi_j(\mathbf{r})$  and a second time for  $\psi_j(\mathbf{r})$  interacting with  $\psi_i(\mathbf{r})$ , as in Eq. (3.8).*

Based on the preceding argument, and using the fact  $J_{ij} > K_{ij}$ , we see that *if you assume the total energy is the sum of the orbital energies, you obtain an energy that is too big.* Indeed, the energy so computed is usually *extremely* poor.

At first, the result in Eq. (3.9) may be counterintuitive: shouldn't the electronic energy of a molecule be the sum of the energies of the composing electrons? Equation (3.9) says this is not the case, but gives us little insight into *why* it is not the case. To make this a bit more clear, suppose his kind students enroll your professor in the local chapter of Misanthropes Anonymous.

### B. The energy it takes to excite an electron from an occupied orbital, $\psi_i(\mathbf{z})$ , to a unoccupied orbital, $\psi_a(\mathbf{z})$ , is not equal to the difference in the orbital energies, $\varepsilon_a - \varepsilon_i$ .

We can approximate the Hartree-Fock wave function for an excited state of the system by replacing an occupied orbital with an unoccupied orbital in the Hartree-Fock wave function, obtaining the Slater determinant

$$\Phi_i^a \equiv |\psi_1 \dots \psi_{i-1} \psi_a \psi_{i+1} \psi_{i+2} \dots \psi_N|. \quad (3.10)$$

Note that this Slater determinant is not stationary with respect to the energy: because of the self-consistency requirement, exciting an electron changes the Fock operator, which causes the orbitals to change. When we skip the self-consistent procedure that produces this “revision” in the orbitals due to the excitation, we say that we have neglected *orbital relaxation*. Neglecting orbital relaxation, the excitation energy can be approximated with



$$E_{exc.}^{i \rightarrow a} \approx \langle \Phi_i^a | \hat{H} | \Phi_i^a \rangle - \langle \Phi_{HF} | \hat{H} | \Phi_{HF} \rangle \quad (3.11)$$

and, using the formula for the energy of a Slater determinant, Eq. (2.92), we obtain

$$\begin{aligned} E_{exc}^{i \rightarrow a} &\approx E_i^a - E_{HF} \\ &\approx \left( \sum_{\substack{k=1 \\ k \neq i}}^N h_k + \frac{1}{2} \sum_{\substack{k=1 \\ k \neq i}}^N \sum_{\substack{l=1 \\ l \neq i}}^N (J_{kl} - K_{kl}) + h_a + \frac{1}{2} \sum_{\substack{l=1 \\ l \neq i}}^N (J_{al} - K_{al}) + \frac{1}{2} \sum_{\substack{k=1 \\ k \neq i}}^N (J_{ka} - K_{ka}) \right) \\ &\quad - \left( \sum_{k=1}^N h_k + \frac{1}{2} \sum_{k=1}^N \sum_{l=1}^N (J_{kl} - K_{kl}) \right) \\ &= \left( h_a + \frac{1}{2} \left( \sum_{l=1}^N (J_{al} - K_{al}) - (J_{ai} - K_{ai}) \right) + \frac{1}{2} \left( \sum_{k=1}^N (J_{ka} - K_{ka}) - (J_{ia} - K_{ia}) \right) \right) \\ &\quad - \left( h_i - \frac{1}{2} \sum_{\substack{k=1 \\ k \neq i}}^N (J_{ki} - K_{ki}) - \frac{1}{2} \sum_{\substack{l=1 \\ l \neq i}}^N (J_{il} - K_{il}) - (J_{ii} - K_{ii}) \right) \\ &= \left( h_a + \sum_{k=1}^N (J_{ka} - K_{ka}) - (J_{ai} - K_{ai}) \right) \\ &\quad - \left( h_i - \sum_{k=1}^N (J_{ki} - K_{ki}) - 0 \right) \\ &= \varepsilon_a - \varepsilon_i - (J_{ai} - K_{ai}) \end{aligned} \quad (3.12)$$

As in the homework problem (problem 5; homework set 3) on the Hartree model, the excitation energy is less than the difference in orbital energies because exciting an electron from an occupied orbital leaves a “vacancy” in the electron distribution the system—a place where electrons are well stabilized (as evidenced by the occupied orbital in that vicinity) but which is, in the excited state, vacant. The excited state orbital is “attracted” to this region, which accounts for the  $J_{ai} - K_{ai}$  term:

$$-(J_{ia} - K_{ia}) \equiv - \iint \frac{|\psi_i(\mathbf{r})|^2 |\psi_a(\mathbf{r}')|}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + \delta_{\sigma_a \sigma_i} \iint \frac{\psi_a^*(\mathbf{r}) \psi_i(\mathbf{r}) \psi_i^*(\mathbf{r}') \psi_a(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'. \quad (3.13)$$

Note that because  $K_{ai} > 0$  unless the spins of the orbitals,  $\psi_a(\mathbf{z})$  and  $\psi_i(\mathbf{z})$ , are different, we conclude that if the  $\alpha$ -spin and  $\beta$ -spin orbitals are the same, as they are for a triplet state, then flipping the spin of the electron (to form a triplet excited state) gives a smaller excitation energy. This predicts that triplet excited states will be more stable than singlet excited states, which is consistent with Hund’s maximum multiplicity rule.

### C. The orbital energy of occupied orbitals are approximations to the ionization potentials of the system.

We can approximate the Hartree-Fock wave function for the stationary states of the cation by removing an occupied orbital from the Hartree-Fock wave function,

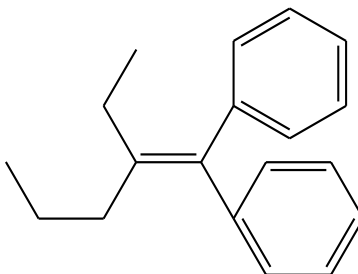
$$\Phi_i^{free} \equiv |\psi_1 \dots \psi_{i-1} \psi_{i+1} \psi_{i+2} \dots \psi_N| \quad (3.14)$$

where the notation indicates that an electron in an occupied orbital,  $\psi_i(\mathbf{r})$  is removed from the system, becoming a “free” (unbound) electron. Neglecting the subsequent relaxation of the remaining occupied orbitals in the cation, we can approximate the ionization of the neutral system to form the excited state of the cation by

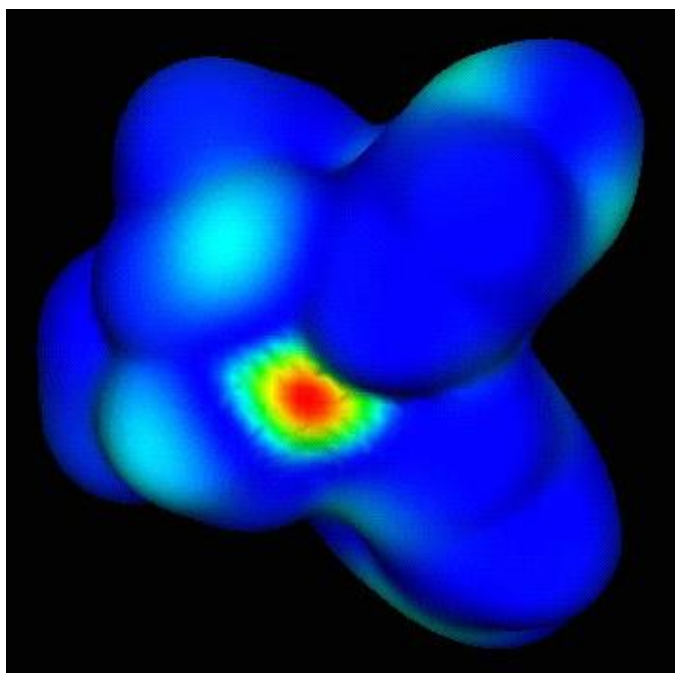
$$\begin{aligned}
 I_i &\approx E_i^{\text{free}} - E_{\text{HF}} \\
 &\approx \sum_{\substack{k=1 \\ k \neq i}}^N h_k + \frac{1}{2} \sum_{\substack{k=1 \\ k \neq i}}^N \sum_{\substack{l=1 \\ l \neq i}}^N (J_{kl} - K_{kl}) - \left( \sum_{k=1}^N h_k + \frac{1}{2} \sum_{k=1}^N \sum_{l=1}^N (J_{kl} - K_{kl}) \right) \\
 &= \left( -h_i - \frac{1}{2} \sum_{\substack{k=1 \\ k \neq i}}^N (J_{ki} - K_{ki}) - \frac{1}{2} \sum_{\substack{l=1 \\ l \neq i}}^N (J_{il} - K_{il}) - (J_{ii} - K_{ii}) \right) \\
 &= - \left( h_i + \sum_{\substack{k=1 \\ k \neq i}}^N (J_{ki} - K_{ki}) \right) - 0 \\
 &= -\varepsilon_i
 \end{aligned} \tag{3.15}$$

The fact that the orbital energies in Hartree-Fock theory approximate the negative of the ionization potentials is called *Koopmans’ theorem*. We can approximate the “way” the electron is removed from the molecule by noting that the electron has been removed from the orbital  $\psi_i(\mathbf{z})$ .

Particularly important for chemical purposes is the highest occupied molecular orbital (HOMO), because  $I_{\text{HOMO}} = -\varepsilon_{\text{HOMO}}$  is the ground state ionization potential: the minimum amount of energy it takes to remove an electron from a molecule. Molecules with large highest-occupied orbital energies (small ionization potentials) are good electron donors/nucleophiles/Lewis bases/reducing agents. The shape of the highest-occupied orbital controls the regioselectivity of the nucleophile: if  $|\psi_{\text{HOMO}}(\mathbf{r})|^2 \approx 0$  at a point, then we observe that it is difficult to remove an electron from the molecule at this point because most of the electron density at this point is associated with electrons in orbitals that are more tightly bound,  $\varepsilon_i < \varepsilon_{\text{HOMO}}$ . For example, the electrophilic attack of borane in the hydroboration reaction of 1,1-diphenyl-2-ethyl-1-butene occurs not on the negatively charged aromatic rings, but at the double bond.



Plotting the square of the highest-occupied orbital energy reveals that this, in fact, is where the most easily ionized electron is localized



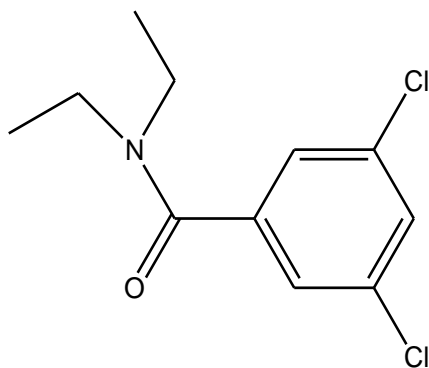
**Figure.** The square of the HOMO orbital for 1,3-diphenyl-2-ethyl-1-butene

#### D. The orbital energy of unoccupied orbitals are approximations to the electron affinities of the system.

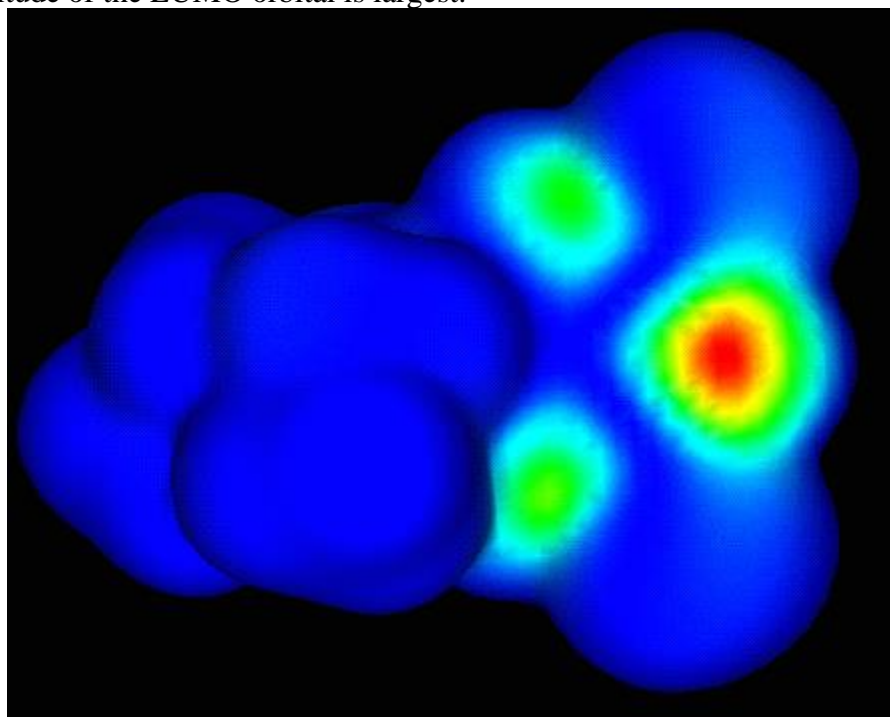
A similar analysis leads to the conclusion that the orbital energies of unoccupied orbitals corresponding to energy gained when an electron is added to the neutral system to form a stationary state (ground or excited) of the anion. That is

$$\begin{aligned} A_{free}^a &\approx E_{HF} - E_{free}^a \\ &\approx -\mathcal{E}_a \end{aligned} \quad (3.16)$$

Koopmans' theorem tends to be much less accurate for electron affinities than ionization potentials but, qualitatively accurate information is often obtained from the unoccupied Hartree-Fock orbitals. This is especially true of the lowest unoccupied orbital, which represents the best way to add an electron to a molecule. Molecules with small lowest unoccupied orbital energies (large electron affinities) tend to be good electron acceptors/electrophiles/Lewis Acids/oxidizing agents. The shape of the lowest-unoccupied orbital controls the regioselectivity of the electrophile: if  $\psi_{LUMO}(\mathbf{r}) \approx 0$ , then adding an electron to the molecule near the point  $\mathbf{r}$  is less energetically favorable, because most of the vacant orbitals in that region have higher orbital energy than the LUMO. For example, one would expect, based on the fact that the carboxamide substituents is a powerful ortho-directing group, that a 3,5-dichloro-tertiary benzamide like the following

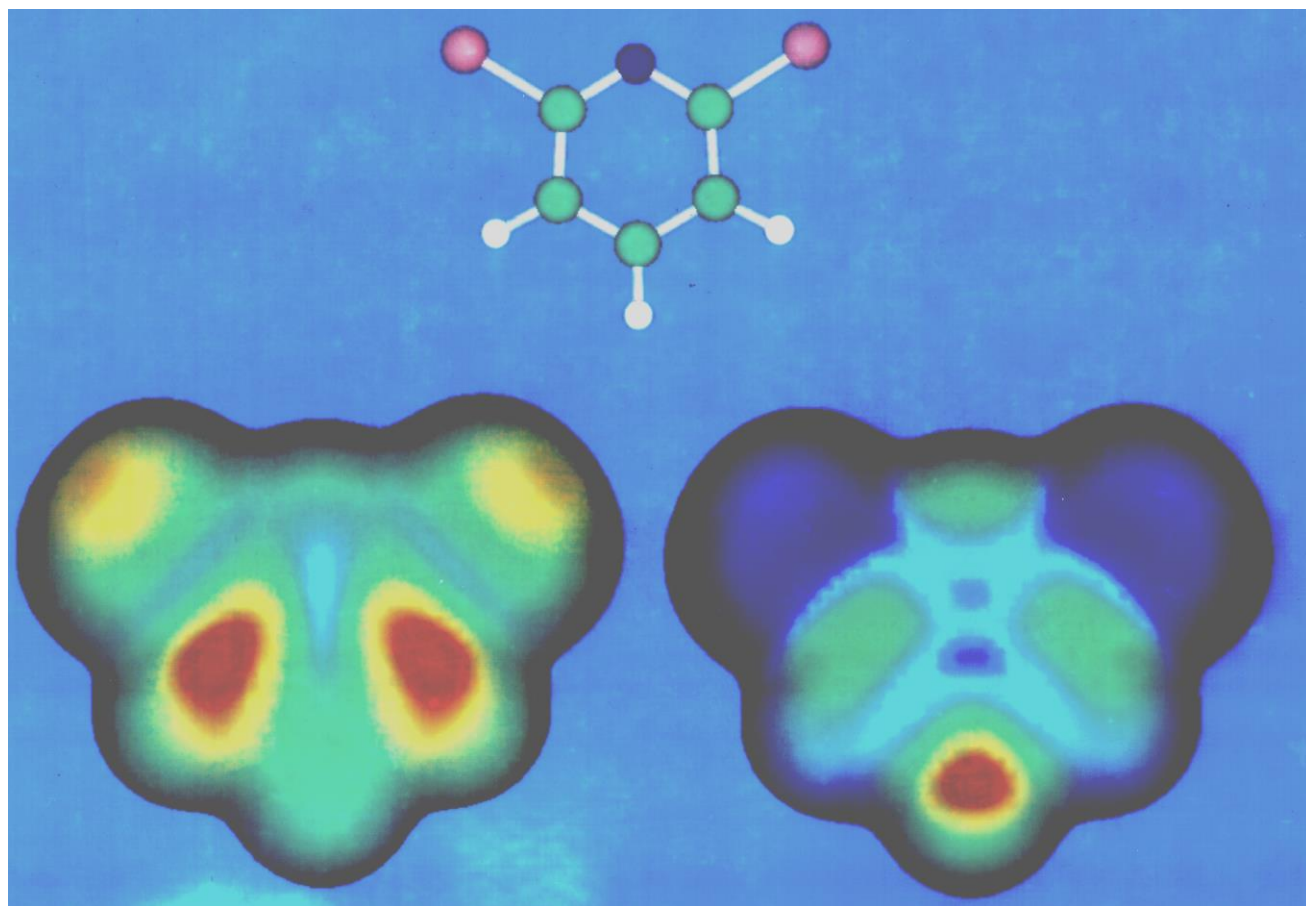


would be subject to metallation (nucleophilic attack) ortho to the carboxamide moiety. However para attack is observed, and this is consistent with the rule that electron donors will attack a complex where the amplitude of the LUMO orbital is largest.



**Figure.** Plot of  $|\psi_{LUMO}(\mathbf{r})|^2$  for a 3,5-dihalogenated benzamide.

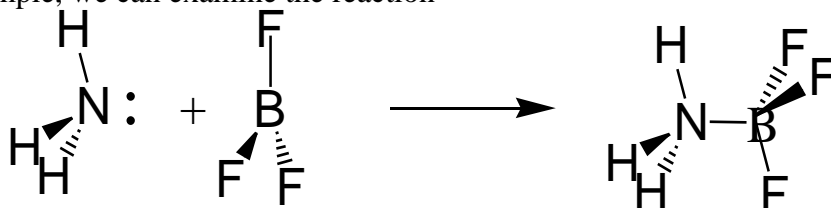
There aren't many compounds that are subject to both nucleophilic and electrophilic attack. One of my favorites is 2,6-dichloropyridine. Most pyridines are not subject to electrophilic attack because electrophilic substitution is usually carried out in rather acidic conditions (electrophiles are Lewis Acids), wherein pyridines are protonated. Because it is difficult to take electrons from a positive species, protonated pyridines are relatively inert to electrophilic attack, and electrophilic aromatic substitution onto pyridines is quite difficult. However, the  $pK_a$  of 2,6-dichloropyridine is -2.86, so this compound usually exists in its unprotonated state. We observe electrophilic attack at the "meta" position and nucleophilic attack (which is much more common, owing to the electronegativity of nitrogen and Chlorine) at the "para" position. These trends are confirmed by the following plots of the LUMO (left) and HOMO (right) orbitals squared, respectively.



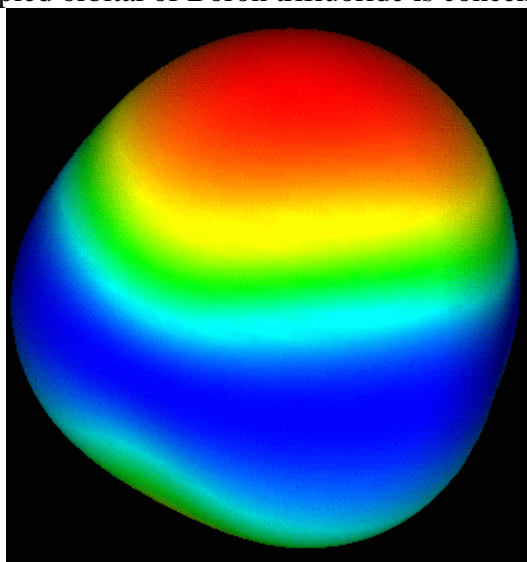
**Figure:**  $|\psi_{LUMO}(\mathbf{r})|^2$  and  $|\psi_{HOMO}(\mathbf{r})|^2$  for 2,6-dichloropyridine.

The preceding analysis is very typical of the utility of the orbital model in chemistry, and Koopmans' theorem can be considered the primary justification for the use of orbitals for describing chemical reactions: most chemical reactions are a combination between electron transfer (ionic binding) and electron sharing (covalent binding) between different molecules. Insofar as this requires “taking electrons” from one molecule and “putting them on another” (and then, if the binding is covalent, replenishing the deficit), the orbitals and orbital energies give an accurate and useful representation of the energetics of chemical processes. For acid-base reactions, the situation is extremely simple. Electrons are removed from the base (from a high-energy occupied orbital) and put on the base (in a low-energy unoccupied orbital). The electrophilic reagent (acid) attacks the nucleophile (base) where the base has “high-energy electrons it is willing to give up”, which is exactly those locations where the orbital amplitudes of the high-energy orbitals are large. The site with which the acid attacks the base is exactly that site at which it can best stabilize the addition electrons: where the orbital magnitude of the vacant orbital is large. This is the essence of the elegantly simple, Nobel-prize-winning insights of Kenichi Fukui.

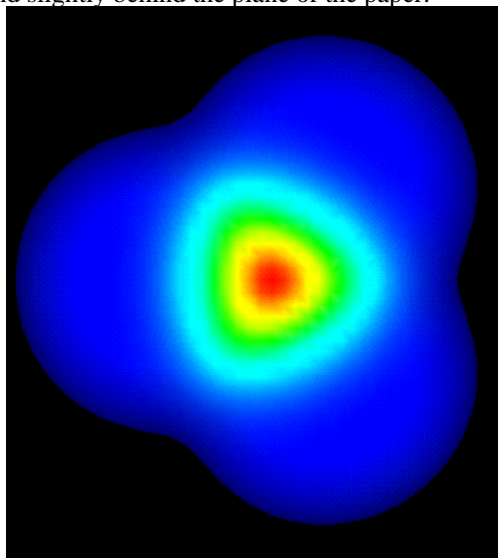
As an example, we can examine the reaction



and note that, as expected, the highest-occupied orbital of ammonia is concentrated on the nitrogen atom while the lowest unoccupied orbital of Boron trifluoride is concentrated on the Boron center.



**Figure.**  $|\psi_{HOMO}(\mathbf{r})|^2$  for ammonia. The red region represents the peak density, and the molecule is oriented with the nitrogens pointed down and slightly behind the plane of the paper.



**Figure.**  $|\psi_{LUMO}(\mathbf{r})|^2$  for  $\text{BF}_3$ . The boron atom is the central atom.

## 4. Propagator (Green's Function) Methods

### I. The Many-Electron Green's Function

Given the obvious utility of the orbitals and orbital energies for chemistry, one may rightly ask whether or not there exists a quantity that can be considered to be the “exact” version of Hartree-Fock theory, with orbital energies that are *exactly* the ionization potentials and electron affinities of the system and “orbitals” that correspond exactly to the change in wave function associated with ionization and electron attachment. There is such a theory, and it is intimately connected to the idea of Green's Functions and Electron Propagators. The general theory of Green's Functions is sketched in this section, and then we discuss the one-electron Green's function and its application to “orbital models” for chemistry in the next section.

To introduce the idea of a Green's function, we consider a classic problem in electrostatics: what is the electrostatic potential,  $\Phi(\mathbf{r})$  due to a charge distribution,  $\mathcal{P}(\mathbf{r})$ . The most fundamental link between the electrostatic potential and the charge distribution is Poisson's equation,

$$\nabla^2 \Phi(\mathbf{r}) = -4\pi \mathcal{P}(\mathbf{r}). \quad (4.1)$$

What we know, of course, is Coulomb's law: the electrostatic potential due to a point charge  $q$  at the point  $\mathbf{x}$  is

$$\Phi(\mathbf{r}) = \frac{q}{|\mathbf{r} - \mathbf{x}|}. \quad (4.2)$$

Similarly, we know that the charge density due to this point charge is

$$\mathcal{P}_{\text{point charge}}(\mathbf{r}) = q\delta(\mathbf{r} - \mathbf{x}) \quad (4.3)$$

and so

$$\nabla^2 \frac{q}{|\mathbf{r} - \mathbf{x}|} = -4\pi q\delta(\mathbf{r} - \mathbf{x}) \quad (4.4)$$

which you will recognize from problem 1 on problem set 1.

The Green's function is defined as the function,  $G(\mathbf{r}, \mathbf{x})$ , such that

$$\nabla^2 G(\mathbf{r}, \mathbf{x}) = -4\pi\delta(\mathbf{r} - \mathbf{x}). \quad (4.5)$$

Why do we care? Well, the Green's functions is typically easy to solve (from Eq. (4.4), we see that  $G(\mathbf{r}, \mathbf{x}) = \frac{1}{|\mathbf{r} - \mathbf{x}|}$ ) because the charge density is so simple. Second, we can write a general charge density using the identity

$$\mathcal{P}(\mathbf{r}) \equiv \int \mathcal{P}(\mathbf{x})\delta(\mathbf{r} - \mathbf{x})d\mathbf{x}. \quad (4.6)$$

To use these results, multiply both sides of Eq. (4.5) by  $\mathcal{P}(\mathbf{x})$  and integrate with respect to  $\mathbf{x}$ .<sup>19</sup>

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<sup>19</sup> In the following equation, we use the fact that *the Laplacian operator operates only on the coordinate  $\mathbf{r}$*  and so, in all but the most pathological cases, it can be pulled outside the integral.

$$\begin{aligned}
\mathcal{P}(\mathbf{x}) \nabla_{\mathbf{r}}^2 G(\mathbf{r}, \mathbf{x}) &= -4\pi \delta(\mathbf{r} - \mathbf{x}) \cdot \mathcal{P}(\mathbf{x}) \\
\nabla_{\mathbf{r}}^2 (G(\mathbf{r}, \mathbf{x}) \mathcal{P}(\mathbf{x})) &= -4\pi \mathcal{P}(\mathbf{x}) \delta(\mathbf{r} - \mathbf{x}) \\
\int \nabla_{\mathbf{r}}^2 (G(\mathbf{r}, \mathbf{x}) \mathcal{P}(\mathbf{x})) d\mathbf{x} &= \int -4\pi \mathcal{P}(\mathbf{x}) \delta(\mathbf{r} - \mathbf{x}) d\mathbf{x} \\
\nabla_{\mathbf{r}}^2 \int (G(\mathbf{r}, \mathbf{x}) \mathcal{P}(\mathbf{x})) d\mathbf{x} &= -4\pi \mathcal{P}(\mathbf{r})
\end{aligned} \tag{4.7}$$

and so

$$\begin{aligned}
\Phi(\mathbf{r}) &\equiv \int \mathcal{P}(\mathbf{x}) G(\mathbf{r}, \mathbf{x}) d\mathbf{x} \\
&= \int \frac{\mathcal{P}(\mathbf{x})}{|\mathbf{x} - \mathbf{r}|} d\mathbf{x}
\end{aligned} \tag{4.8}$$

and we have turned the difficult task of solving a inhomogeneous partial differential equation into a comparatively simple exercise in integration.

The Schrödinger equation is not, in its usual formulation, an inhomogeneous differential equation but is, instead, an eigenvalue problem,

$$\hat{H}\Psi = E\Psi \tag{4.9}$$

or

$$(E - \hat{H})\Psi = 0 \tag{4.10}$$

which rather resembles a homogeneous partial differential equation, and so resembles the inhomogeneous Poisson equation as much as any form we are likely to find. So, by analogy to Eq. (4.5), we define the Green's function,  $G(\boldsymbol{\tau}, \boldsymbol{\tau}'; E)$  to satisfy the equation

$$(E - \hat{H}(\boldsymbol{\tau}))G(\boldsymbol{\tau}, \boldsymbol{\tau}'; E) = \delta(\boldsymbol{\tau} - \boldsymbol{\tau}') \tag{4.11}$$

where we have used  $\boldsymbol{\tau}$  to denote the coordinates (both spatial and spin) for all the electrons in the molecule. The solution to Eq. (4.11) is given by

$$G(\boldsymbol{\tau}, \boldsymbol{\tau}'; E) \equiv \sum_{k=0}^{\infty} \frac{\Psi_k(\boldsymbol{\tau}) \Psi_k^*(\boldsymbol{\tau}')}{E - E_k} \tag{4.12}$$

where  $\Psi_k$  and  $E_k$  are the eigenfunctions and eigenvalues of the Hamiltonian. Equation (4.12) is easily verified by direct substitution into Eq. (4.11)

$$\begin{aligned}
(E - \hat{H}(\boldsymbol{\tau})) \sum_{k=0}^{\infty} \frac{\Psi_k(\boldsymbol{\tau}) \Psi_k^*(\boldsymbol{\tau}')}{E - E_k} &= \sum_{k=0}^{\infty} \frac{(E - \hat{H}(\boldsymbol{\tau})) \Psi_k(\boldsymbol{\tau}) \Psi_k^*(\boldsymbol{\tau}')}{E - E_k} \\
&= \sum_{k=0}^{\infty} \frac{(E \Psi_k(\boldsymbol{\tau}) - \hat{H}(\boldsymbol{\tau}) \Psi_k(\boldsymbol{\tau})) \Psi_k^*(\boldsymbol{\tau}')}{E - E_k} \\
&= \sum_{k=0}^{\infty} \frac{(E \Psi_k(\boldsymbol{\tau}) - E_k \Psi_k(\boldsymbol{\tau})) \Psi_k^*(\boldsymbol{\tau}')}{E - E_k} \\
&= \sum_{k=0}^{\infty} \frac{(E - E_k) \Psi_k(\boldsymbol{\tau}) \Psi_k^*(\boldsymbol{\tau}')}{E - E_k} \\
&= \sum_{k=0}^{\infty} \Psi_k(\boldsymbol{\tau}) \Psi_k^*(\boldsymbol{\tau}') \\
&= \delta(\boldsymbol{\tau} - \boldsymbol{\tau}')
\end{aligned} \tag{4.13}$$



where the last step is taken from equation I.3 in problem set 1.

There are a couple very useful properties of the Green's function that bear mention. The first occurs when we know the Green's function for one Hamiltonian,  $\hat{H}_0$ , but we do not know the Green's function for the Hamiltonian of interest,  $\hat{H} = \hat{H}_0 + \hat{V}$ . Then, defining

$$(E - \hat{H}_0)G_0(\tau, \tau'; E) = \delta(\tau - \tau') \quad (4.14)$$

we can find the Green's function for the system of interest by manipulation of the defining Eq. (4.11). That is,

$$\begin{aligned} (E - \hat{H}(\tau))G(\tau, \tau'; E) &= \delta(\tau - \tau') \\ (E - (\hat{H}_0(\tau) - \hat{V}(\tau)))G(\tau, \tau'; E) &= \delta(\tau - \tau') \\ (E - \hat{H}_0)G(\tau, \tau'; E) &= \delta(\tau - \tau') + \hat{V}G(\tau, \tau'; E) \end{aligned} \quad (4.15)$$

$$\begin{aligned} G_0(\tau'', \tau, E)(E - \hat{H}_0(\tau))G(\tau, \tau'; E) &= G_0(\tau'', \tau, E) \begin{pmatrix} \delta(\tau - \tau') \\ +\hat{V}(\tau)G(\tau, \tau'; E) \end{pmatrix} \\ \int G_0(\tau'', \tau, E)(E - \hat{H}_0(\tau))G(\tau, \tau'; E) d\tau &= \int G_0(\tau'', \tau, E) \begin{pmatrix} \delta(\tau - \tau') \\ +\hat{V}(\tau)G(\tau, \tau'; E) \end{pmatrix} d\tau \end{aligned}$$

Defining the eigenvalues and eigenvectors for the known Hamiltonian as  $\hat{H}\Psi_k^{(0)}(\tau) = E_k\Psi_k^{(0)}(\tau)$  we have, using the Hermitian property of the Hamiltonian and the resolution of the Green's functions in terms of its eigenfunctions, Eq. (4.12), that

$$\begin{aligned} \int G_0(\tau'', \tau, E)(E - \hat{H}_0(\tau))G(\tau, \tau'; E) d\tau &= \int G_0(\tau'', \tau, E) \begin{pmatrix} \delta(\tau - \tau') \\ +\hat{V}(\tau)G(\tau, \tau'; E) \end{pmatrix} d\tau \\ \int \sum_{k=0}^{\infty} \frac{\Psi_k^{(0)}(\tau'')(\Psi_k^{(0)}(\tau))^*}{E - E_k^{(0)}} (E - \hat{H}_0(\tau))G(\tau, \tau'; E) d\tau &= G_0(\tau'', \tau', E) + \int G_0(\tau'', \tau, E)\hat{V}(\tau)G(\tau, \tau'; E) d\tau \\ \int \left( \sum_{k=0}^{\infty} \frac{(E - \hat{H}_0(\tau))\Psi_k^{(0)}(\tau'')(\Psi_k^{(0)}(\tau))^*}{E - E_k^{(0)}} \right) G(\tau, \tau'; E) d\tau &= G_0(\tau'', \tau', E) + \int G_0(\tau'', \tau, E)\hat{V}(\tau)G(\tau, \tau'; E) d\tau \quad (4.16) \\ \int \left( \sum_{k=0}^{\infty} \Psi_k^{(0)}(\tau'')(\Psi_k^{(0)}(\tau))^* \right) G(\tau, \tau'; E) d\tau &= G_0(\tau'', \tau', E) + \int G_0(\tau'', \tau, E)\hat{V}(\tau)G(\tau, \tau'; E) d\tau \\ \int \delta(\tau'' - \tau)G(\tau, \tau'; E) d\tau &= G_0(\tau'', \tau', E) + \int G_0(\tau'', \tau, E)\hat{V}(\tau)G(\tau, \tau'; E) d\tau \\ G(\tau'', \tau', E) &= G_0(\tau'', \tau', E) + \int G_0(\tau'', \tau, E)\hat{V}(\tau)G(\tau, \tau'; E) d\tau \end{aligned}$$

Equation (4.16) is an elegant application of perturbation theory, and allows one express the Green's function for an "unknown" system as a "correction" to one you have already computed.

Once you have the Green's function, you can find anything you want to know about your system. Most important, of course, are the eigenvalues and eigenfunctions. The eigenvalues are

found by finding the *poles* of the Green's function:<sup>20</sup>  $G(\tau, \tau'; E)$  becomes infinite when  $E$  is equal to an eigenvalue, as is apparent from Eq. (4.12). There are several elegant ways to get information about the eigenvectors (and other properties of various states of the system) using complex analysis, but, from (4.12), it is obvious that we can find the eigenvalues by taking the limit

$$\begin{aligned}\Psi_k(\tau)\Psi_k^*(\tau') &= \lim_{E \rightarrow E_k} (E - E_k)G(\tau, \tau'; E) \\ &= \lim_{E \rightarrow E_k} \sum_{j=0}^{\infty} \frac{(E - E_k)\Psi_j(\tau)\Psi_j^*(\tau')}{E - E_j} \\ &= \lim_{E \rightarrow E_k} \frac{(E - E_k)\Psi_k(\tau)\Psi_k^*(\tau')}{E - E_k} + \lim_{E \rightarrow E_k} \sum_{\substack{j=0 \\ j \neq k}}^{\infty} \frac{(E - E_k)\Psi_j(\tau)\Psi_j^*(\tau')}{E - E_j} \\ &= \Psi_k(\tau)\Psi_k^*(\tau') + 0\end{aligned}\tag{4.17}$$

(Equation (4.17) must be slightly revised for a degenerate state.)

To keep with the theme of finding the “neat properties” of the Green's function, we write the energy as a frequency,

$$\begin{aligned}\omega &= \frac{E}{\hbar} \\ \omega_k &= \frac{E_k}{\hbar}.\end{aligned}\tag{4.18}$$

Then we have,

$$\begin{aligned}G(\tau, \tau'; E) &\equiv \sum_{k=0}^{\infty} \frac{\Psi_k(\tau)\Psi_k^*(\tau')}{E - E_k} \\ &= \sum_{k=0}^{\infty} \frac{\Psi_k(\tau)\Psi_k^*(\tau')}{\hbar\left(\frac{E}{\hbar} - \frac{E_k}{\hbar}\right)} \\ &= \frac{1}{\hbar} \sum_{k=0}^{\infty} \frac{\Psi_k(\tau)\Psi_k^*(\tau')}{(\omega - \omega_k)} \\ &= \frac{1}{\hbar} G(\tau, \tau'; \omega)\end{aligned}\tag{4.19}$$

where we have defined, in analogy to Eq. (4.12),

$$G(\tau, \tau'; \omega) \equiv \sum_{k=0}^{\infty} \frac{\Psi_k(\tau)\Psi_k^*(\tau')}{(\omega - \omega_k)}.\tag{4.20}$$

Taking the Fourier transform with respect to frequency of  $G(\tau, \tau'; \omega)$  (see section 9 in the sixth set of notes), we have

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<sup>20</sup> When a function,  $f(z)$ , resembles  $\frac{A}{(z-z_0)^k}$  near  $z_0$ , we say that the function has a  $k^{th}$  order pole at  $z_0$  with *residue*  $A$ . We see that the Green's function has poles at the energy eigenvalues of the system, the order of the pole is equal to the degeneracy of the state, and the residue is equal to a sum over the eigenfunctions of the state ( $g$  is the level of degeneracy),  $\sum_{i=1}^g \Psi_i(\tau)\Psi_i^*(\tau')$ . When  $g = 1$ , the eigenvalue is nondegenerate and we say that we have a “simple” pole. To find the poles of the Green's function, we need to find values of  $E$  where the Green's function becomes infinite.

$$\begin{aligned}
\mathcal{G}(\tau, \tau'; t) &\equiv \int_{-\infty}^{\infty} e^{i\omega t} G(\tau, \tau'; \omega) d\omega \\
&= \int_{-\infty}^{\infty} e^{i\omega t} \left( \sum_{k=0}^{\infty} \frac{\Psi_k(\tau) \Psi_k^*(\tau')}{(\omega - \omega_k)} \right) d\omega \\
&= \sum_{k=0}^{\infty} \Psi_k(\tau) \Psi_k^*(\tau') \int_{-\infty}^{\infty} \frac{e^{i\omega t}}{(\omega - \omega_k)} d\omega
\end{aligned} \tag{4.21}$$

To evaluate the integral, we use the known result (from a table of Fourier transforms) that

$$\text{sgn}(t) = -2i \int_{-\infty}^{\infty} \frac{e^{i\omega t}}{\omega} d\omega. \tag{4.22}$$

The inverse Fourier transform in Eq. (4.21) can then be performed:

$$\begin{aligned}
\int_{-\infty}^{\infty} \frac{e^{i\omega t}}{(\omega - \omega_k)} d\omega &= e^{i\omega_k t} \int_{-\infty}^{\infty} \frac{e^{i(\omega - \omega_k)t}}{\omega - \omega_k} d\omega \\
&= e^{i\omega_k t} \int_{-\infty}^{\infty} \frac{e^{i(\omega - \omega_k)t}}{\omega - \omega_k} d(\omega - \omega_k) \\
&= e^{i\omega_k t} \left( \frac{-1}{2i} \right) \text{sgn}(t) \\
&= \frac{i}{2} e^{i\omega_k t} \text{sgn}(t).
\end{aligned} \tag{4.23}$$

and so

$$\begin{aligned}
\mathcal{G}(\tau, \tau'; t) &\equiv \int_{-\infty}^{\infty} e^{i\omega t} G(\tau, \tau'; \omega) d\omega \\
&= \frac{i}{2} \text{sgn}(t) \sum_{k=0}^{\infty} \Psi_k(\tau) \Psi_k^*(\tau') e^{i\omega_k t}
\end{aligned} \tag{4.24}$$

Differentiating Eq. (4.24) with respect to time gives

$$\frac{\partial \mathcal{G}(\tau, \tau'; t)}{\partial t} \equiv \frac{i}{2} \sum_{k=0}^{\infty} \Psi_k(\tau) \Psi_k^*(\tau') e^{i\omega_k t} \frac{\partial \text{sgn}(t)}{\partial t} + \frac{i}{2} \text{sgn}(t) \sum_{k=0}^{\infty} \Psi_k(\tau) \Psi_k^*(\tau') (i\omega_k) e^{i\omega_k t} \tag{4.25}$$

There is a “trick” for differentiating  $\text{sgn}(t)$ . Note that

$$\begin{aligned}
\int_{-\infty}^x \delta(x) dx &= \begin{cases} 0 & x < 0 \\ 1 & x > 0 \end{cases} \\
&\equiv \eta(x)
\end{aligned} \tag{4.26}$$

The right-hand-side of this equation,  $\eta(x)$ , is called the “Heaviside” function. Using the fundamental theorem of calculus, we see that  $\delta(x) = \frac{d\eta(x)}{dx}$  and, from the definition of the Heaviside function, we have

$$\begin{aligned}
2\eta(x) - 1 &= \begin{cases} -1 & x < 0 \\ 1 & x > 0 \end{cases} \\
&\equiv \text{sgn}(x).
\end{aligned} \tag{4.27}$$

It follows that

$$\frac{d \operatorname{sgn}(t)}{dt} = 2\delta(t) \quad (4.28)$$

and so, returning to Eq. (4.25),

$$\begin{aligned} \frac{\partial \mathcal{G}(\tau, \tau'; t)}{\partial t} &= \frac{i}{2} \sum_{k=0}^{\infty} \Psi_k(\tau) \Psi_k^*(\tau') e^{i\omega_k t} \frac{\partial \operatorname{sgn}(t)}{\partial t} + \frac{i}{2} \operatorname{sgn}(t) \sum_{k=0}^{\infty} \Psi_k(\tau) \Psi_k^*(\tau') (i\omega_k) e^{i\omega_k t} \\ &= \frac{i}{2} (2\delta(t)) \sum_{k=0}^{\infty} \Psi_k(\tau) \Psi_k^*(\tau') e^{i\omega_k t} + \frac{i}{2} \left( \frac{i}{\hbar} \right) \operatorname{sgn}(t) \sum_{k=0}^{\infty} E_k \Psi_k(\tau) \Psi_k^*(\tau') e^{i\omega_k t} \end{aligned} \quad (4.29)$$

We can set  $t = 0$  in the first term since the first term will be zero anyway (due to the  $\delta(t)$  factor) when this is not true. So

$$\begin{aligned} \frac{\partial \mathcal{G}(\tau, \tau'; t)}{\partial t} &= \frac{i}{2} (2\delta(t)) \sum_{k=0}^{\infty} \Psi_k(\tau) \Psi_k^*(\tau') e^{i\omega_k(0)} + \frac{i}{2} \left( \frac{i}{\hbar} \right) \operatorname{sgn}(t) \sum_{k=0}^{\infty} \hat{H} \Psi_k(\tau) \Psi_k^*(\tau') e^{i\omega_k t} \\ &= \frac{i}{2} (2\delta(t)) \sum_{k=0}^{\infty} \Psi_k(\tau) \Psi_k^*(\tau') + \frac{i}{\hbar} \hat{H} \mathcal{G}(\tau, \tau'; t) \\ &= i\delta(\tau - \tau') \delta(t) + \frac{i}{\hbar} \hat{H} \mathcal{G}(\tau, \tau'; t) \end{aligned} \quad (4.30)$$

Finally, we have that

$$\begin{aligned} \frac{\hbar}{i} \frac{\partial \mathcal{G}(\tau, \tau'; t)}{\partial t} &= \hat{H} \mathcal{G}(\tau, \tau'; t) + \hbar \delta(\tau - \tau') \delta(t) \\ -i\hbar \frac{\partial \mathcal{G}(\tau, \tau'; t)}{\partial t} - \hat{H} \mathcal{G}(\tau, \tau'; t) &= \hbar \delta(\tau - \tau') \delta(t) \end{aligned} \quad (4.31)$$

which resembles the equation we expect a time-dependent Green's function to satisfy. In particular, the time-dependent Schrödinger equation is usually written

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H} \Psi \quad (4.32)$$

or

$$-i\hbar \frac{\partial \Psi^*}{\partial t} = \hat{H} \Psi^* \quad (4.33)$$

and so we sometimes use the time-dependent Green's function defined by

$$G(\tau, \tau'; t) \equiv \frac{1}{\hbar} (\mathcal{G}(\tau, \tau'; t))^* = \frac{1}{2\pi} \int_{-\infty}^{\infty} G(\tau, \tau'; E) e^{-iEt} dt \quad (4.34)$$

because this function satisfies the simpler equation

$$i\hbar \frac{\partial G(\tau, \tau'; t)}{\partial t} - \hat{H} G(\tau, \tau'; t) = \delta(\tau - \tau') \delta(t). \quad (4.35)$$

Regarding Eq. (4.24), it is clear that the time-dependent Green's function is related to the propagator:

$$K(\tau, \tau'; t) = \sum_{k=0}^{\infty} \Psi_k(\tau) e^{-iE_k t / \hbar} \Psi_k^*(\tau'). \quad (4.36)$$

Given a wave function,  $\Phi(\tau')$ , at  $t = 0$ , the wave function at other times is just

$$\Phi(\tau, t) = \sum_{k=0}^{\infty} c_k \Psi_k(\tau) e^{-iE_k t / \hbar}. \quad (4.37)$$

If the Hamiltonian is independent of time, the expansion coefficients do not change in time, and can be determined at  $t = 0$  with the usual method,

$$c_k \equiv \langle \Psi_k | \Phi_k \rangle. \quad (4.38)$$

Consequently,

$$\begin{aligned} \int K(\tau, \tau'; t) \Phi(\tau'; 0) d\tau' &= \sum_{k=0}^{\infty} \Psi_k(\tau) e^{-iE_k t/\hbar} \langle \Psi_k^*(\tau') | \Phi(\tau'; 0) \rangle \\ &= \sum_{k=0}^{\infty} c_k \Psi_k(\tau) e^{-iE_k t/\hbar} \\ &= \Phi(\tau'; t). \end{aligned} \quad (4.39)$$

That is, the function  $K(\tau, \tau'; t)$  “propagates” an “initial” wave function at  $t = 0$  to other times of interest.

## II. The One-Electron Green’s Function

From the previous section, hopefully you have gleaned that the Green’s function is a powerful tool, containing a wealth of useful information and a number of useful properties. However, solving Eq. (4.11) for the Green’s function is just as hard (even a bit harder) than solving the full Schrödinger equation. For this reason, various scientists have proposed a number of “one-electron” Green’s functions, each of which is appropriate for specific sorts of processes. There are Green’s functions that are very appropriate for describing excitation processes, for example, but the most common Green’s functions used in chemistry are those appropriate to describing ionization and electron affinity.

Based on Eq. (4.12), we might write the Hartree-Fock Green’s function as

$$G_{HF}(\mathbf{z}, \mathbf{z}'; \varepsilon) \equiv \sum_{k=1}^{\infty} \frac{\psi_k(\mathbf{z}) \psi_k^*(\mathbf{z}')}{\varepsilon - \varepsilon_k} \quad (4.40)$$

where  $\varepsilon_k$  and  $\psi_k(\mathbf{z})$  are the  $k^{th}$  eigenvalue and eigenfunction of the Hartree-Fock equation. Equation (4.40) is the Green’s function for the one-electron Hamiltonian used to solve the Hartree-Fock equations

$$\hat{f}(\mathbf{r}) \psi_{\alpha}(\mathbf{z}) \equiv \left( -\frac{\nabla^2}{2} + v(\mathbf{r}) + j(\mathbf{r}) - \hat{k}(\mathbf{z}) \right) \psi_{\alpha}(\mathbf{z}) = \varepsilon_{\alpha} \psi_{\alpha}(\mathbf{z}); \quad (4.41)$$

compare Eq. (2.137).

For an  $N$ -electron atom, the first  $N$  orbitals are occupied, so we might rewrite Eq. (4.40) as

$$\begin{aligned} G_{HF}(\mathbf{z}, \mathbf{z}'; \varepsilon) &\equiv \sum_{k=1}^N \frac{\psi_k(\mathbf{z}) \psi_k^*(\mathbf{z}')}{\varepsilon - \varepsilon_k} + \sum_{k=N+1}^{\infty} \frac{\psi_k(\mathbf{z}) \psi_k^*(\mathbf{z}')}{\varepsilon - \varepsilon_k} \\ &= \sum_{k=1}^N \frac{\psi_k(\mathbf{z}) \psi_k^*(\mathbf{z}')}{\varepsilon - \varepsilon_k} + \sum_{l=1}^{\infty} \frac{\psi_{N+l}(\mathbf{z}) \psi_{N+l}^*(\mathbf{z}')}{\varepsilon - \varepsilon_{N+l}} \end{aligned} \quad (4.42)$$

Remember Koopmans’ Theorem: the orbitals and orbital energies in the first sum are approximations to the electron removal (ionization) process, while the orbitals and orbital energies in the second sum are approximations to the electron attachment process.

As the final result we need to “review” from Hartree-Fock theory, remember that the energy can be computed in terms of the orbital energies. In particular, comparing Eq. (3.8),

$$\sum_{i=1}^N \varepsilon_i \equiv \sum_{i=1}^N \left( h_i + \sum_{j=1}^N (J_{ij} - K_{ij}) \right) \quad (4.43)$$

to Eq. (3.7),

$$E_{HF} \equiv \sum_{i=1}^N \left( h_i + \frac{1}{2} \sum_{j=1}^N (J_{ij} - K_{ij}) \right). \quad (4.44)$$

we recognize that

$$\begin{aligned} 2E_{HF} &= \sum_{i=1}^N \varepsilon_i + \sum_{i=1}^N h_i \\ &= \sum_{i=1}^N (\varepsilon_i + h_i). \end{aligned} \quad (4.45)$$

We want to find the “exact” analogue to these results for the Hartree-Fock Green’s function. There are a lot of elegant results we shall not be able to cover, and a lot of derivations we cannot consider, mostly because they require complex analysis (and, in particular, the methods of residue integration). However, we can define and explore the properties of the exact one-electron Green’s function. To do this, we

- remember that the occupied orbital energies are approximately equal to the negative of the various ionization energies of the system ( $\varepsilon_k \approx -I_k$ ). This suggests that the “exact” Green’s function will have  $(\varepsilon + I_k)$  instead of  $(\varepsilon - \varepsilon_k)$  in the denominator of the first term.
- remember that the unoccupied orbital energies are approximately equal to the negative of various electron affinities of the system ( $\varepsilon_{l+N} \approx -A_l$ ). This suggests that we will have  $(\varepsilon + A_l)$  instead of  $(\varepsilon - \varepsilon_{l+N})$  in the denominator of the second term.
- remember that Hartree-Fock occupied orbitals reflect “where an electron came from”. It is specifically useful that

$$\begin{aligned} \langle \psi_1 \dots \psi_{N-1} | | \psi_1 \dots \psi_N \rangle_{1\dots N-1} &= \iiint \dots \int (|\psi_1 \psi_2 \dots \psi_{N-1}|)^* |\psi_1 \dots \psi_N| d\mathbf{z}_1 \dots d\mathbf{z}_{N-1} \\ &= \frac{1}{\sqrt{N}} \psi_N(\mathbf{z}_N) \end{aligned} \quad (4.46)$$

where the factor of  $\frac{1}{\sqrt{N}}$  comes from the fact that the normalization constant for an  $N$ -electron Slater determinant is  $\frac{1}{\sqrt{N!}}$ , but the normalization constant for an  $(N-1)$ -electron Slater determinant is  $\frac{1}{\sqrt{(N-1)!}} = \frac{\sqrt{N}}{\sqrt{N!}}$ . From a different perspective, we require that the orbital

should be normalized. However we have no right to specify that it is the  $N^{\text{th}}$  electron that will be removed (as we did in Eq. (4.46)), so that the total “electron loss due to ionization” is the probability that the electron lost was electron 1, plus the probability it was electron 2, ... plus the probability the electron removed was electron  $N$ . The total probability, then, is the  $N$ -times the probability of the removal of a single electron, and so

$$|\psi_N(\mathbf{z})|^2 \equiv N \left| \langle \psi_1 \dots \psi_{N-1} | | \psi_1 \dots \psi_N \rangle_{1\dots N-1} \right|^2 \quad (4.47)$$

which also implies Eq. (4.46).

Based on Eq. (4.46), we recognize that the exact place an electron comes from during various electron removal processes can be expressed in terms of the various wave functions for the cation,  $\Psi_k^{(N-1)}(\mathbf{z}_1, \dots, \mathbf{z}_{N-1})$ , and the ground state of the neutral system,  $\Psi_0^{(N)}(\mathbf{z}_1, \dots, \mathbf{z}_N)$ , in analogy to Eq. (4.46), namely,

$$g_k(\mathbf{z}) \equiv \sqrt{N} \iiint \dots \int \left( \Psi_k^{(N-1)}(\mathbf{z}_1, \dots, \mathbf{z}_{N-1}) \right)^* \Psi_0^{(N)}(\mathbf{z}_1, \dots, \mathbf{z}_{N-1}, \mathbf{z}) d\mathbf{z}_1 \dots d\mathbf{z}_{N-1}. \quad (4.48)$$

We expect that these *Dyson orbitals*, which are also called the *generalized overlap amplitudes* and *Feynman-Dyson orbitals* (or amplitudes), will replace the Hartree-Fock orbitals in the first sum in Eq. (4.42).

- Using the same sort of arguments, we have that

$$\begin{aligned} \langle \psi_1 \dots \psi_N | | \psi_1 \dots \psi_N \psi_{N+1} \rangle_{1\dots N} &= \iiint \dots \int (|\psi_1 \dots \psi_N|)^* |\psi_1 \dots \psi_N \psi_{N+1}| d\mathbf{z}_1 \dots d\mathbf{z}_N \\ &= \frac{1}{\sqrt{N+1}} \psi_{N+1}(\mathbf{z}_{N+1}) \end{aligned} \quad (4.49)$$

We guess, then, that the unoccupied orbitals in the second term of Eq. (4.42) will be replaced by

$$f_l(\mathbf{z}) \equiv \sqrt{N+1} \iiint \dots \int \left( \Psi_0^{(N)}(\mathbf{z}_1, \dots, \mathbf{z}_{N-1}) \right)^* \Psi_l^{(N+1)}(\mathbf{z}_1, \dots, \mathbf{z}_N, \mathbf{z}) d\mathbf{z}_1 \dots d\mathbf{z}_N \quad (4.50)$$

These orbitals are also called generalized overlap amplitudes, or Feynman-Dyson orbitals.

Using these insights, and defining the ionization potentials and electron affinities of the system with

$$I_k \equiv E_k^{(N-1)} - E_0^{(N)} \quad (4.51)$$

and

$$A_l \equiv E_0^{(N)} - E_l^{(N+1)} \quad (4.52)$$

respectively, we have that the exact one-electron Green's function is given by

$$G(\mathbf{z}, \mathbf{z}'; \varepsilon) \equiv \sum_{k=0}^{\infty} \frac{g_k(\mathbf{z}) g_k^*(\mathbf{z}')}{\varepsilon + I_k} + \sum_{l=0}^{\infty} \frac{f_l(\mathbf{z}) f_l^*(\mathbf{z}')}{\varepsilon + A_l}. \quad (4.53)$$

The reader will not be surprised that the one-electron Green's function and, in particular, the Feynman-Dyson orbitals, are the “right” quantities to use when describing chemical processes and, in particular, electron transfer between reagents.

In general the Green's function is used for interpretation of chemical results and spectra, but the exact ground-state energy can be computed from it using an analogue of Eq. (4.45). We have that

$$2E_0^{(N)} = \sum_{k=0}^{\infty} -\langle g_k | g_k \rangle I_k + \sum_{k=1}^{\infty} \sum_{l=1}^{\infty} \langle g_k | g_l \rangle \langle g_l | \hat{h} | g_k \rangle \quad (4.54)$$

This expression is more complicated than the expression for the Hartree-Fock orbitals. The reason is that the Dyson orbitals are not, in general, orthonormal:

$$\langle g_k | g_l \rangle \neq \delta_{kl} \quad (\text{except for exceptional cases}). \quad (4.55)$$

Note that, if we take  $-I_k = \varepsilon_k$  and assume that only  $N$  Dyson orbitals are occupied, and that these orbitals are orthonormal, then we regain the Hartree-Fock form, Eq. (4.45).

The only reason the Green's function is not used more in chemistry calculations is that it is relatively difficult to accurately compute. The most popular method for computation is to use the generalization of the Hartree-Fock equations, Eq. (3.1), wherein:

$$\left\{ -\frac{\nabla^2}{2} + v(\mathbf{r}) + j(\mathbf{r}) - \hat{k}(\mathbf{z}) + \hat{\Sigma}(I_k, \mathbf{z}) \right\} g_k(\mathbf{z}) \equiv (-I_k) g_k(\mathbf{z}) \quad (4.56)$$

$\hat{\Sigma}(\varepsilon, \mathbf{z})$  is called the *self-energy* of the electron,<sup>21</sup> and in general it depends on the energy of the state under consideration (owing to the dependence on  $\varepsilon$  in Eq. (4.53)). Now, referring to Eq. (4.16), we

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<sup>21</sup> Sometimes the self energy is defined so that it includes other terms, notably the Coulomb and exchange terms in the potential. Technically, then, we should call  $\hat{\Sigma}(\varepsilon, \mathbf{z})$  the “self-energy of correlation.”

can write the exact Green's function in terms of the Hartree-Fock Green's function (which is easily computed from Eq. (4.42)) and the self energy, namely,

$$G(\mathbf{z}, \mathbf{z}', \varepsilon) \equiv G_{HF}(\mathbf{z}, \mathbf{z}', \varepsilon) + \int G_{HF}(\mathbf{z}, \mathbf{x}, \varepsilon) \hat{\Sigma}(\varepsilon, \mathbf{x}) G(\mathbf{x}, \mathbf{z}', \varepsilon) d\mathbf{x}. \quad (4.57)$$

One might think, then, that computing the exact Green's function is not very difficult. This would be incorrect. The self-energy is a very, very complicated function. (An expression for the self-energy can be derived from Eq. (V.10) in homework set 2, which is just Eq. (4.56) derived in a more straightforward way. This equation should give you some idea of the complexity involved in computing the self-energy when you don't know the eigenfunctions of the cation ahead of time.)

Look at Eq. (4.57) (or Eq. (4.56)). Assuming the self-energy term is zero regains the Hartree-Fock equations and the Hartree-Fock Green's functions. Given that the exact Green's function is the exact representation of ionization and electron attachment, and is the "best" representation of electron transfer (that is, acid/base chemistry) and cooperative electron processes (bonding) in molecules, we surmise that the only reason the Hartree-Fock orbitals and orbital energies are useful in chemistry is that they resemble the Dyson orbitals and exact ionization potentials/electron affinities. That is, the orbitals and orbital energies that are typically used to describe chemical processes "inherit" their usefulness from the "exact" descriptors, which are computed using the one-electron Green's function.

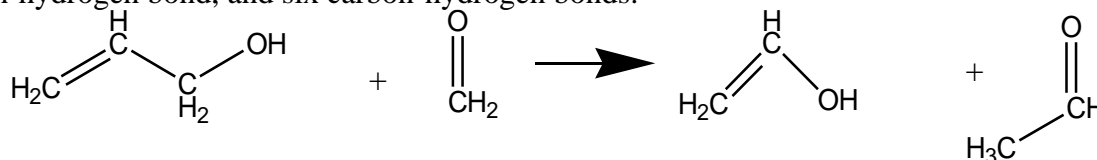


## 5. Treating Electron Correlation as a Correction to the Hartree-Fock Method

### I. The Importance of Electron Correlation

Often Hartree-Fock theory is simply not accurate enough. A good rule of thumb is that the correlation energy—defined as the error in the Hartree-Fock approach, is of the order of 1 eV ( $\approx 100 \frac{\text{kJ}}{\text{mol}}$ ) per (valence) electron pair. This leads to the obvious conclusion that, for chemistry, Hartree-Fock is just not good enough.

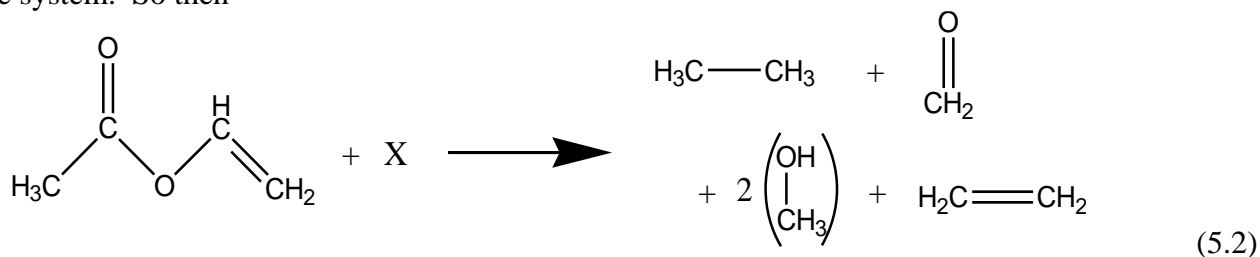
This, however, is not quite true. One can use Hartree-Fock quite usefully if one keeps in mind its limitations, what it is good for, and devotes oneself to studying processes for which the errors due to the neglect of cancellation almost cancel themselves out. In particular, many workers have studied isodesmic reactions, wherein the number and type of bonds on each side of the reaction remains unchanged. These are especially useful for computing thermodynamic properties (e.g., the heat of formation and heat of reaction) because one can always write the decomposition of a large molecule into a small molecule as an isodesmic reaction. A good Hartree-Fock calculation can often estimate the heat of formation of a compound to within a few kcal/mol. For example, the following reaction is isodesmic because both reactants and products have one carbon-carbon double bond, one carbon-carbon single bond, one carbon-oxygen double bond, one carbon-oxygen single bond, one oxygen-hydrogen bond, and six carbon-hydrogen bonds.



As an example of how one computes a heat of formation using an isodesmic reaction, we consider

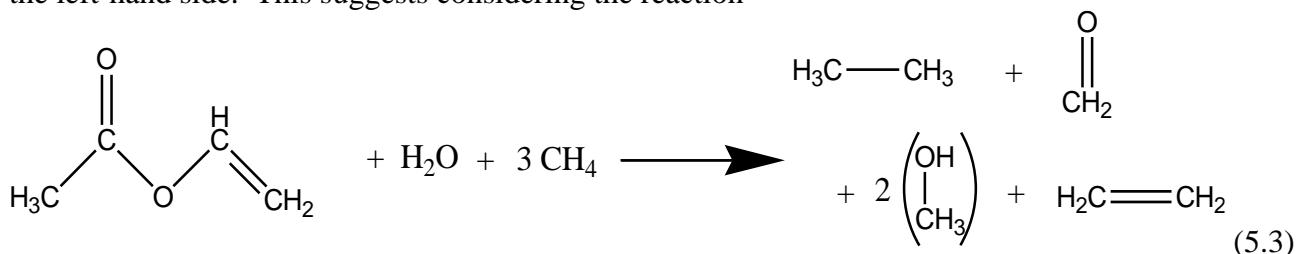


The “goal” is to write this reagent as a “sum of small compounds” for which thermochemical data will be available. One way to do this is to consider a “bond dissociation reaction”, wherein we consider the products to be the species with the “chemical” (that is, not bonds to hydrogen) bonds in the system. So then



where  $X$  is chosen to balance the equation. Counting up the numbers of O-H and C-H bonds, we see that there are 6 C-H bonds on the left-hand side of the equation and 18 on the right-hand side of

the equation. Similarly, there are two O-H bonds on the right hand side of the equation but none of the left-hand side. This suggests considering the reaction



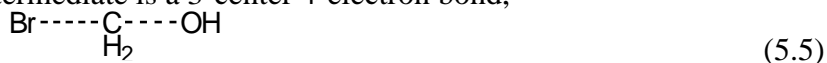
which is seen to be balanced. Using this general method, one can compute any reaction energy using an isodesmic reaction. In general, every time you compute a reaction energy—even when you are not using the Hartree-Fock method—you should use isodesmic reactions.

There are some cases, however, when we must go beyond Hartree-Fock. Let me list a few examples:

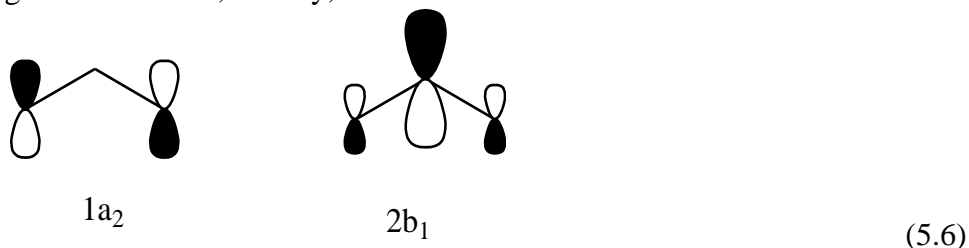
- Predict the dissociation energy of Lithium Hydride. (Hard because an “ionic” molecule is dissociating into neutral species.)
- Predict the rate of the  $S_N2$  reaction,



(Difficult because the intermediate is a 3-center 4-electron bond,

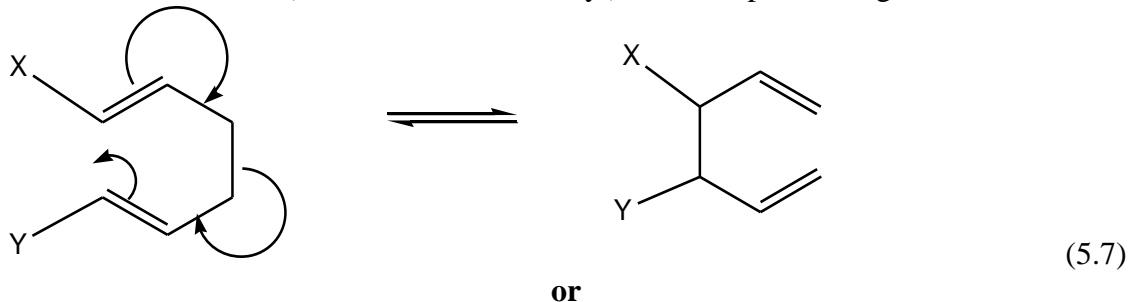


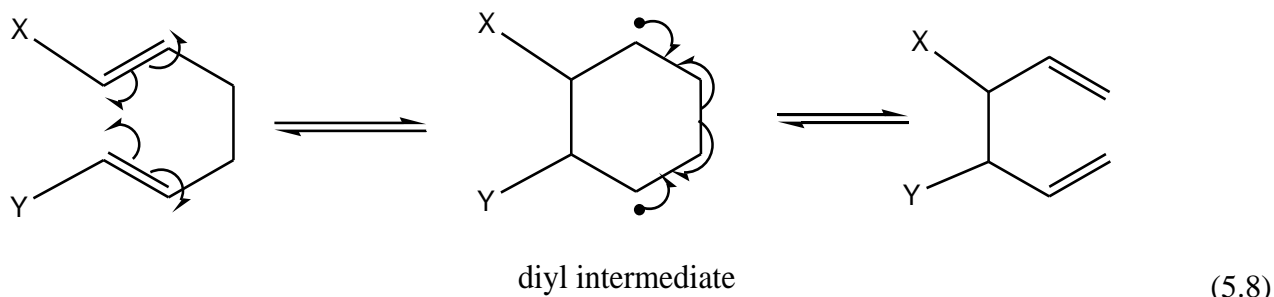
- Predict the spectrum (both vibrational and electronic) of ozone. (Hard because there are two almost degenerate orbitals, namely,



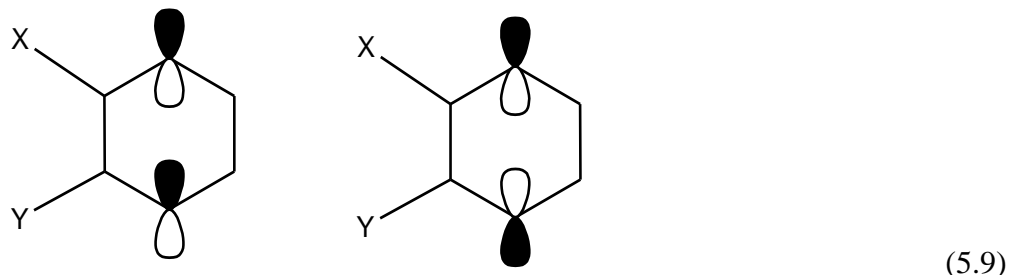
(To get an idea of the problems this introduces: for a long time, the computed binding energy of the Ozone molecule  $D_e$ , was about .6 eV, while the observed value was .5 eV greater than this.)

- Predict the mechanism (concerted or the 1,4-diyl) of the Cope rearrangement,





Hard—especially the diyl-intermediate possibility—because there are two almost degenerate orbitals,



- Predict whether a given cation forms a thiocyanate (bonds to  $\text{SCN}^-$  through the sulfur atom) or an isothiocyanate (bonds to  $\text{SCN}^-$  through the nitrogen atom). (Requires the local hard/soft acid/base principle.)

In each of these cases, the desired accuracy exceeds that which we can routinely achieve with Hartree-Fock. Take, for example, the determination of the reaction rate for the  $S_N2$  reaction. To achieve this goal, we need to accurately determine the activation energy of the reaction, and the rate will then be proportional to

$$\text{rate} \propto e^{-E_a/kT}. \quad (5.10)$$

An order-of-magnitude error in the rate then corresponds to a very small error indeed:

$$(10)^{\pm 1} \cdot \text{rate} = e^{-(E_a + \varepsilon)/kT}$$

$$\pm \ln(10) + \ln(\text{rate}) = \frac{-E_a}{kT} - \frac{\varepsilon}{kT} \quad (5.11)$$

$$\varepsilon = \pm kT \ln(10)$$

$$\approx .002 \text{ Hartree}$$

in the activation energy. (Boltzmann's constant is  $315800 \frac{\text{°K}}{\text{Hartree}}$ .) This is more than we can hope for with Hartree-Fock, with the correlation energy error being proportional (approximately) to the number of binding electron pairs formed and broken, giving errors an order of magnitude larger than this.

## II. Configuration Interaction

We *define* the error in the Hartree-Fock model as being due to electron correlation, and we define the correlation energy as

$$E_{\text{corr}} = E_{\text{exact}} - E_{\text{HF}} \quad (5.12)$$

Because the Hartree-Fock energy is always above the exact energy, the correlation energy is always negative,

$$E_{\text{corr}} < 0. \quad (5.13)$$

Why do we call the error in the Hartree-Fock model the correlation energy? Let us define the *Hartree-Fock Hamiltonian*,

$$\hat{F} \equiv \sum_{i=1}^N \hat{f}(\mathbf{r}_i) \quad (5.14)$$

where the Fock operator,  $\hat{f}(\mathbf{r}_i)$ , is defined in Eq. (2.139). Recall, however, that when a Hamiltonian takes the form of a sum of one-electron Hamiltonians that the energy eigenvalue is just the sum of the one-electron Hamiltonians energies and that the wave function is just a product of the one-electron wave functions, so that

$$\hat{F}\psi_{i_1}(\mathbf{z}_1)\psi_{i_2}(\mathbf{z}_2)\dots\psi_{i_N}(\mathbf{z}_N) = \sum_{k=1}^N \varepsilon_{i_k} \psi_{i_1}(\mathbf{z}_1)\psi_{i_2}(\mathbf{z}_2)\dots\psi_{i_N}(\mathbf{z}_N) \quad (5.15)$$

where  $\{\psi_{i_k}\}$  and  $\{\varepsilon_{i_k}\}$  are any of the Hartree-Fock orbitals. Of course, the Hartree-product wave function in Eq. (5.15) neither respects the indistinguishability of electrons nor the antisymmetry principle, but a linear combination of these wave functions—the Slater determinant—does:

$$\hat{F}|\psi_{i_1}\psi_{i_2}\dots\psi_{i_N}| = \left(\sum_{k=1}^N \varepsilon_{i_k}\right)|\psi_{i_1}\psi_{i_2}\dots\psi_{i_N}|. \quad (5.16)$$

The eigenfunctions of  $\hat{F}$  that are appropriate for indistinguishable Fermions—like electrons—are the Slater determinants, and because  $\hat{F}$  is a Hamiltonian, which is a Hermitian operator, these eigenfunctions form a complete set. We conclude that we can, by considering all the possible ways of forming a Slater determinant of Hartree-Fock orbitals, obtain a complete set of functions in terms of which the exact wave function can be expanded.

We also note that there are no  $\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$  terms in the Hartree-Fock Hamiltonian—there are no terms explicitly linking the distance between the electrons. In the Hartree-Fock Hamiltonian: electrons only interact with the “average position” of the other electrons, and there is no “explicit” and “direct” Coulomb repulsion between electrons. Similarly, if we ignore the requirement of antisymmetry, the Hartree product wave function suggests that electrons move entirely independent—the wave function of the total system is merely the product of the wave functions for each electron, and so the probability of observing electron 1 at  $\mathbf{r}_1$ , electron 2 at  $\mathbf{r}_2$ , etc. is just the product of the probability that electron 1 is at  $\mathbf{r}_1$ , electron 2 is at  $\mathbf{r}_2$ , etc., with all electrons moving entirely independently:

$$|\psi_1(\mathbf{z}_1)\psi_2(\mathbf{z}_2)\dots\psi_N(\mathbf{z}_N)|^2 = |\psi_1(\mathbf{z}_1)|^2 |\psi_2(\mathbf{z}_2)|^2 \dots |\psi_N(\mathbf{z}_N)|^2 \quad (5.17)$$

The probability electron 1 is at  $\mathbf{r}_1$  is unaffected by whether or not electron 2 is at  $\mathbf{r}_2$ . When we move from the Hartree-product description to the Slater determinant description, matters are complicated, but similar. In particular, the probability that there is an electron with spin  $\alpha$  at  $\mathbf{x}$  and an electron with spin  $\beta$  at  $\mathbf{x}'$  can be computed as

$$\rho_2(\mathbf{x}, \alpha; \mathbf{x}', \beta) = \left\langle |\psi_1 \dots \psi_N| \left| \sum_{i=1}^{N-1} \sum_{j=i+1}^N \delta_{\sigma_i \alpha} \delta(\mathbf{r}_i - \mathbf{x}) \delta_{\sigma_j \beta} \delta(\mathbf{r}_j - \mathbf{x}') \right| |\psi_1 \dots \psi_N| \right\rangle \quad (5.18)$$

which is similar in form to the 2-electron electron-electron repulsion integral, and can be evaluated using Eq. (2.68),

$$\begin{aligned}
& \left\langle \left| \psi_1 \psi_2 \dots \psi_N \right| \left[ \sum_{i=1}^N \sum_{j=1}^N \delta_{\sigma_i \alpha} \delta(\mathbf{r}_i - \mathbf{x}) \delta_{\sigma_j \beta} \delta(\mathbf{r}_j - \mathbf{x}') \right] \left| \psi_1 \psi_2 \dots \psi_N \right| \right\rangle \\
&= \sum_{i=1}^{N-1} \sum_{j=1}^N \left[ \left\langle \psi_i(\mathbf{z}_1) \psi_j(\mathbf{z}_2) \left| \delta_{\sigma_i \alpha} \delta(\mathbf{r}_1 - \mathbf{x}) \delta_{\sigma_j \beta} \delta(\mathbf{r}_2 - \mathbf{x}') \right| \psi_i(\mathbf{z}_1) \psi_j(\mathbf{z}_2) \right\rangle \right. \\
&\quad \left. - \left\langle \psi_i(\mathbf{z}_1) \psi_j(\mathbf{z}_2) \left| \delta_{\sigma_i \alpha} \delta(\mathbf{r}_1 - \mathbf{x}) \delta_{\sigma_j \beta} \delta(\mathbf{r}_2 - \mathbf{x}') \right| \psi_j(\mathbf{z}_1) \psi_i(\mathbf{z}_2) \right\rangle \right] \\
&= \sum_{i=1}^N \sum_{j=1}^N |\psi_i(\mathbf{x})|^2 |\psi_j(\mathbf{x}')|^2 \delta_{\sigma_i \alpha} \delta_{\sigma_j \beta} \\
&= \left( \sum_{i=1}^N \delta_{\sigma_i \alpha} |\psi_i(\mathbf{x})|^2 \right) \left( \sum_{i=1}^N \delta_{\sigma_i \beta} |\psi_i(\mathbf{x}')|^2 \right)
\end{aligned} \tag{5.19}$$

which is just the product of the probability of observing an  $\alpha$ -spin electron at  $\mathbf{x}$  and that of observing a  $\beta$ -spin electron at  $\mathbf{x}'$ . When the electrons have the same spin things are slightly more complicated (the second term in the second line in Eq. (5.19) need not be zero), and we have, for example,

$$\begin{aligned}
& \left\langle \left| \psi_1 \psi_2 \dots \psi_N \right| \left[ \sum_{i=1}^N \sum_{j=1}^N \delta_{\sigma_i \alpha} \delta(\mathbf{r}_i - \mathbf{x}) \delta_{\sigma_j \alpha} \delta(\mathbf{r}_j - \mathbf{x}') \right] \left| \psi_1 \psi_2 \dots \psi_N \right| \right\rangle \\
&= \sum_{i=1}^{N-1} \sum_{j=1}^N \left[ \left\langle \psi_i(\mathbf{z}_1) \psi_j(\mathbf{z}_2) \left| \delta_{\sigma_i \alpha} \delta(\mathbf{r}_1 - \mathbf{x}) \delta_{\sigma_j \alpha} \delta(\mathbf{r}_2 - \mathbf{x}') \right| \psi_i(\mathbf{z}_1) \psi_j(\mathbf{z}_2) \right\rangle \right. \\
&\quad \left. - \left\langle \psi_i(\mathbf{z}_1) \psi_j(\mathbf{z}_2) \left| \delta_{\sigma_i \alpha} \delta(\mathbf{r}_1 - \mathbf{x}) \delta_{\sigma_j \alpha} \delta(\mathbf{r}_2 - \mathbf{x}') \right| \psi_j(\mathbf{z}_1) \psi_i(\mathbf{z}_2) \right\rangle \right] \\
&= \sum_{i=1}^N \sum_{j=1}^N |\psi_i(\mathbf{x})|^2 |\psi_j(\mathbf{x}')|^2 \delta_{\sigma_i \alpha} \delta_{\sigma_j \alpha} - \sum_{i=1}^N \sum_{j=1}^N \psi_i^*(\mathbf{x}) \psi_i(\mathbf{x}') \psi_j(\mathbf{x}) \psi_j^*(\mathbf{x}') \delta_{\sigma_i \alpha} \delta_{\sigma_j \alpha} \\
&= \left( \sum_{i=1}^N \delta_{\sigma_i \alpha} |\psi_i(\mathbf{x})|^2 \right) \left( \sum_{i=1}^N \delta_{\sigma_i \alpha} |\psi_i(\mathbf{x}')|^2 \right) - \sum_{i=1}^N \sum_{j=1}^N \psi_i^*(\mathbf{x}) \psi_i(\mathbf{x}') \psi_j(\mathbf{x}) \psi_j^*(\mathbf{x}') \delta_{\sigma_i \alpha} \delta_{\sigma_j \alpha}.
\end{aligned} \tag{5.20}$$

A small amount of correlation between same spin electrons, then is introduced by requiring that no two electrons with the same spin can be at the same place (Pauli exclusion principle), but we usually call this very special sort of “correlation” between the electrons “exchange”, and reserve the term “correlation” to mean the more sophisticated collective electron motions that represent corrections to both Eqs. (5.19) and (5.20).

How can we include correlation effects? Recall the variational principle:

$$E_0 \equiv \min_{\Psi} \langle \Psi | \hat{H} | \Psi \rangle \tag{5.21}$$

(we assume the wave function is normalized). *We can get the exact ground state energy and exact ground-state wave function, including electron correlation effects, by minimizing the energy with respect to all normalized, antisymmetric, wave functions.* Unfortunately, test *all* the normalized wave functions more than we can manage. A simple choice was to take a Slater determinant of orbitals, and this gave us the Hartree-Fock equations. However, there are certainly cases (e.g., the ozone molecule or a diyl intermediate) where, because several Slater determinants are very close together in energy, we expect that describing our system with a single Slater determinant will be a poor approximation. In this case, we might take a cue from the configuration interaction method we used to improve the molecular-orbital approximation to the hydrogen molecule and helium atom—write the wave function as a sum of several Slater determinants,

$$\Psi = \sum_k c_k \Phi_k \quad (5.22)$$

Recall that given a Hermitian operator, the set of all eigenfunctions of that operator forms a complete, orthonormal, set. That is, if we consider a complete set of Slater determinants, then the expansion in Eq. (5.22) will be *exact*. (We used the same trick in perturbation theory, for example, when we wrote the wave function for the “perturbed” system as a linear combination of the wave functions of the “unperturbed” system.) In the *configuration interaction* method, we choose, along the lines of the previous discussion, all the possible Slater determinants of Hartree-Fock orbitals,

$$\Psi_{exact} \equiv \sum_{\substack{\text{all Slater} \\ \text{dets. of HF} \\ \text{orbitals}}} c_k \Phi_k \quad (5.23)$$

We expect that the “largest component” will be the ground state Hartree-Fock wave function. Often the other coefficients in Eq. (5.23) are very small.

In order to keep track of all the possible Hartree-Fock orbitals, we often write the ground-state Hartree-Fock wave function as  $\Phi_0$ , the Slater determinant with an electron “excited” from the  $i^{\text{th}}$  occupied orbital to the  $a^{\text{th}}$  unoccupied orbital as  $\Phi_i^a$ , the “doubly-excited” Slater determinants as  $\Phi_{ij}^{ab}$ , etc.. With this notation, we can write the exact wave function as

$$\begin{aligned} \Psi = & c_0 \Phi_0 + \underbrace{\sum_{i=1}^N \sum_{a=N+1}^K c_i^a \Phi_i^a}_{\text{single excitations (S)}} + \underbrace{\sum_{i>j=1}^N \sum_{a>b=N+1}^K c_{ij}^{ab} \Phi_{ij}^{ab}}_{\text{double excitations (D)}} \\ & + \underbrace{\sum_{i>j>k=1}^N \sum_{a>b>c=N+1}^K c_{ijk}^{abc} \Phi_{ijk}^{abc}}_{\text{triple excitations (T)}} + \underbrace{\sum_{i>j>k>l=1}^N \sum_{a>b>c>d=N+1}^K c_{ijkl}^{abcd} \Phi_{ijkl}^{abcd}}_{\text{quadruple excitations (Q)}} + \dots \end{aligned} \quad (5.24)$$

The inequality signs reflect the fact that all that matters (to within a negative sign) is the orbitals that are occupied. For example, all of the following excitations describe the same doubly-excited state:  $\Phi_{ij}^{ab} = -\Phi_{ji}^{ab} = -\Phi_{ij}^{ba} = \Phi_{ji}^{ba}$ .

Because, in practice, one can never compute ALL the unoccupied Hartree-Fock orbitals, the upper limit in the sum is designed to indicate that there are only  $K$  occupied orbitals. It should be clear that the number of terms in this expansion grows *very* rapidly as we consider higher-and-higher levels of excitation.

Sometimes it is helpful to abbreviate the indices on the Slater determinants by introducing vectors,  $\mathbf{i}$  and  $\mathbf{a}$ , whose components are the orbitals from which an electron is removed ( $i_1, i_2, \dots$ ) and the orbitals to which it is excited ( $a_1, a_2, \dots$ ), respectively. If  $i_k = a_k$ , then there is no excitation at all from orbital  $\psi_{i_k}(\mathbf{r})$ . By convention, we group the electrons that are excited at the beginning of the vector, so that

$$\begin{aligned}
\Psi = & c_{[1,2,3,\dots,N]}^{[1,2,3,\dots,N]} \Phi_{[1,2,3,\dots,N]}^{[1,2,3,\dots,N]} + \underbrace{\sum_{i_1=1}^N \sum_{a=N+1}^K c_{[i_1,i_2,\dots,i_N]}^{[a_1,i_2,\dots,i_N]} \Phi_{[i_1,i_2,\dots,i_N]}^{[a_1,i_2,\dots,i_N]}}_{\text{single excitations (S)}} + \underbrace{\sum_{i_1>i_2=1}^N \sum_{a_1>a_2=N+1}^K c_{[i_1,i_2,i_3,\dots,i_N]}^{[a_1,a_2,i_3,\dots,i_N]} \Phi_{[i_1,i_2,i_3,\dots,i_N]}^{[a_1,a_2,i_3,\dots,i_N]}}_{\text{double excitations (D)}} \\
& + \underbrace{\sum_{i_1>i_2>i_3=1}^N \sum_{a_1>a_2>a_3=N+1}^K c_{[i_1,i_2,i_3,i_4,\dots,i_N]}^{[a_1,a_2,a_3,i_4,\dots,i_N]} \Phi_{[i_1,i_2,i_3,i_4,\dots,i_N]}^{[a_1,a_2,a_3,i_4,\dots,i_N]}}_{\text{triple excitations (T)}} \\
& + \underbrace{\sum_{i_1>i_2>i_3>i_4=1}^N \sum_{a_1>a_2>a_3>a_4=N+1}^K c_{[i_1,i_2,i_3,i_4,i_5,\dots,i_N]}^{[a_1,a_2,a_3,a_4,i_5,\dots,i_N]} \Phi_{[i_1,i_2,i_3,i_4,i_5,\dots,i_N]}^{[a_1,a_2,a_3,a_4,i_5,\dots,i_N]}}_{\text{quadruple excitations (Q)}} + \dots \\
= & \sum_{\mathbf{i}, \mathbf{a}} c_{\mathbf{i}}^{\mathbf{a}} \Phi_{\mathbf{i}}^{\mathbf{a}}
\end{aligned} \tag{5.25}$$

To compute the configuration interaction wave function, we start with the Schrödinger equation,

$$H\Psi = E\Psi. \tag{5.26}$$

Next, we multiply both sides by a Slater determinant,  $\Phi_{\mathbf{i}}^{\mathbf{a}}$ :

$$\Phi_{\mathbf{i}}^{\mathbf{a}} \hat{H} \Psi = \Phi_{\mathbf{i}}^{\mathbf{a}} E \Psi. \tag{5.27}$$

Next, we substitute in the form we are using for the wave function, Eq. (5.25), so that

$$\Phi_{\mathbf{i}}^{\mathbf{a}} \hat{H} \sum_{\mathbf{j}, \mathbf{b}} c_{\mathbf{j}}^{\mathbf{b}} \Phi_{\mathbf{j}}^{\mathbf{b}} = E \Phi_{\mathbf{i}}^{\mathbf{a}} \sum_{\mathbf{j}, \mathbf{b}} c_{\mathbf{j}}^{\mathbf{b}} \Phi_{\mathbf{j}}^{\mathbf{b}} \tag{5.28}$$

and integrate, obtaining

$$\begin{aligned}
\sum_{\mathbf{j}, \mathbf{b}} \langle \Phi_{\mathbf{i}}^{\mathbf{a}} | \hat{H} | \Phi_{\mathbf{j}}^{\mathbf{b}} \rangle c_{\mathbf{j}}^{\mathbf{b}} &= E \sum_{\mathbf{j}, \mathbf{b}} \langle \Phi_{\mathbf{i}}^{\mathbf{a}} | \Phi_{\mathbf{j}}^{\mathbf{b}} \rangle c_{\mathbf{j}}^{\mathbf{b}} \\
&= E \sum_{\mathbf{j}, \mathbf{b}} \delta_{\mathbf{ij}} \delta_{\mathbf{ab}} c_{\mathbf{j}}^{\mathbf{b}} \\
&= E c_{\mathbf{i}}^{\mathbf{a}}
\end{aligned} \tag{5.29}$$

Recalling that the “component form” for the matrix eigenvalue problem,  $\mathbf{A}\mathbf{c} = \alpha\mathbf{c}$  is just

$$\sum_{j=1}^n A_{ij} c_j = \alpha c_i, \tag{5.30}$$

we recognize that Eq. (5.29) is just a matrix eigenvalue problem, with the Hamiltonian matrix being

$$H_{\mathbf{i}, \mathbf{j}}^{\mathbf{a}, \mathbf{b}} \equiv \langle \Phi_{\mathbf{i}}^{\mathbf{a}} | \hat{H} | \Phi_{\mathbf{j}}^{\mathbf{b}} \rangle. \tag{5.31}$$

Finding the lowest-energy eigenvalue from

$$\sum_{\mathbf{i}, \mathbf{a}} H_{\mathbf{i}, \mathbf{j}}^{\mathbf{a}, \mathbf{b}} c_{\mathbf{j}}^{\mathbf{b}} = E c_{\mathbf{i}}^{\mathbf{a}} \tag{5.32}$$

is entirely equivalent to minimizing the energy with respect to all wave functions with the form of Eq. (5.25).

Of course, we will need to truncate the expansion in Eq. (5.25), and not consider any excitations above some order. When we truncate at zeroth-order, we have the Hartree-Fock method. At first order, we have “Configuration-Interaction with Single excitations” (CIS), at second order we

have “Configuration Interaction with Single and Double excitations” (CISD), and so on: CISDT (third order), CISDTQ (fourth order), .... When we do not truncate the expansion (so that we include  $N$ -electron excitations) we say we are doing a Full-Configuration-Interaction calculations, which is called Full-CI (FCI). Full configuration interaction calculations are very, very costly, and their cost is related to the binomial coefficient<sup>22</sup>

$$\binom{K}{N} \equiv \frac{(K)!}{(K-N)!N!} \quad (5.33)$$

where  $K$  is the total number of Hartree-Fock orbitals that were solved for and  $N$  is the number of electrons. For sufficiently large  $K$ , Full-CI calculations are essentially exact. The success of all other forms of computation tends to be measured based on “how close to Full-CI” they are.

We now consider the possible ways to truncate the expansion.

### a. Single Excitations Only (CIS)

When this series is truncated at “zeroth” order, we have the Hartree-Fock method. One might expect that the “next best thing” would be to truncate the expansion at first-order, including only the single excitations. This method is called “configuration interaction singles” (CIS) and is occasionally used for excited states. However, there is a result called Brillouin’s theorem:

**Brillouin’s Theorem:**

$$\langle \Phi_i^a | \hat{H} | \Phi_0 \rangle = 0 \quad (5.34)$$

which implies that there including the single excitations does not help use describe the ground state. (Brillouin’s theorem implies that the Hamiltonian cannot “induce single-excitations” from the Hartree-Fock determinant, and so there is no correction from the single-excitations alone.

To see this in more detail, we consider the Hartree-Fock wave function,  $\Phi_1^1$  and just two single excited states,  $\Phi_1^2$  and  $\Phi_1^3$ . Then the CIS wave function is

$$\Psi_{CIS} \equiv c_1^1 \Phi_1^1 + c_1^2 \Phi_1^2 + c_1^3 \Phi_1^3. \quad (5.35)$$

Examining Eq. (5.32), it is clear that we need to solve the eigenvalue problem

$$\begin{bmatrix} \langle \Phi_1^1 | \hat{H} | \Phi_1^1 \rangle & \langle \Phi_1^1 | \hat{H} | \Phi_1^2 \rangle & \langle \Phi_1^1 | \hat{H} | \Phi_1^3 \rangle \\ \langle \Phi_1^2 | \hat{H} | \Phi_1^1 \rangle & \langle \Phi_1^2 | \hat{H} | \Phi_1^2 \rangle & \langle \Phi_1^2 | \hat{H} | \Phi_1^3 \rangle \\ \langle \Phi_1^3 | \hat{H} | \Phi_1^1 \rangle & \langle \Phi_1^3 | \hat{H} | \Phi_1^2 \rangle & \langle \Phi_1^3 | \hat{H} | \Phi_1^3 \rangle \end{bmatrix} \begin{bmatrix} c_1^1 \\ c_1^2 \\ c_1^3 \end{bmatrix} = E \begin{bmatrix} c_1^1 \\ c_1^2 \\ c_1^3 \end{bmatrix} \quad (5.36)$$

and, from Brillouin’s theorem, we have that all the integrals between the Hartree-Fock wave function and the singly excited states are zero, so

$$\begin{bmatrix} H_{1,1}^{1,1} & 0 & 0 \\ 0 & H_{1,1}^{2,2} & H_{1,1}^{2,3} \\ 0 & (H_{1,1}^{2,3})^* & H_{1,1}^{3,3} \end{bmatrix} \begin{bmatrix} c_1^1 \\ c_1^2 \\ c_1^3 \end{bmatrix} = E \begin{bmatrix} c_1^1 \\ c_1^2 \\ c_1^3 \end{bmatrix} \quad (5.37)$$

---

<sup>22</sup> The cost is actually a good bit less than this, owing to the fact that configurations with different spins and symmetries do not affect one another. However, the factorial nature of the cost is inherent in full configuration interaction.



which has the eigenvalues

$$E_0 = H_{1,1}^{1,1} \equiv E_{HF}$$

$$E_{1,2} = \frac{H_{1,1}^{2,2} + H_{1,1}^{3,3}}{2} \pm \frac{1}{2} \sqrt{\left(H_{1,1}^{2,2} - H_{1,1}^{3,3}\right)^2 + 4 \left|H_{1,1}^{2,3}\right|^2} \quad (5.38)$$

That is, while there is no correction to the ground state energies, there is a correction to the Hartree-Fock excitation energies—an improvement over Eq. (3.12). Because CIS calculations are not that difficult, they are commonly used for computing excitation energies. This is sometimes called the Tamm-Dancoff approximation by people who like to sound obscure.

A CIS calculation, then, can be denoted “symbolically” as:

$$\begin{bmatrix} H_{i,i}^{i,i} & 0 & 0 \\ 0 & H_{i,i}^{a,a} & H_{i,j}^{a,b} \\ 0 & (H_{i,j}^{a,b})^* & H_{j,j}^{b,b} \end{bmatrix} \begin{bmatrix} c_i^i \\ c_i^a \\ c_i^b \end{bmatrix} = E \begin{bmatrix} c_i^i \\ c_i^a \\ c_i^b \end{bmatrix} \quad (5.39)$$

where  $i, j$  are confined to the occupied orbitals, while  $a, b$  are restricted to the unoccupied orbitals.

## A. Single + Double Excitations, CISD

The only type of excited state Slater determinant that interacts with the Hartree-Fock wave function *directly* is the double excitations, where

$$\langle \Phi_{HF} | \hat{H} | \Phi_{i,j}^{a,b} \rangle \equiv \langle \psi_i \psi_j | \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} | \psi_a \psi_b \rangle - \langle \psi_i \psi_j | \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} | \psi_b \psi_a \rangle. \quad (5.40)$$

We can consider the easy case where we consider one single and one double excitation, so that

$$\Psi \approx c_{i_1 i_2}^{i_1 i_2} \Phi_{i_1 i_2}^{i_1 i_2} + c_{i_1 i_2}^{a_1 i_2} \Phi_{i_1 i_2}^{a_1 i_2} + c_{i_1 i_2}^{a_1 a_2} \Phi_{i_1 i_2}^{a_1 a_2} \quad (5.41)$$

and we find the coefficients by solving the eigenvalue problem

$$\begin{bmatrix} H_{i_1 i_2; i_1 i_2}^{i_1 i_2; i_1 i_2} & 0 & H_{i_1 i_2; i_1 a_2}^{i_1 i_2; i_1 a_2} \\ 0 & H_{i_1 i_2; i_1 i_2}^{a_1 i_2; a_1 i_2} & H_{i_1 i_2; i_1 i_2}^{a_1 i_2; a_1 a_2} \\ (H_{i_1 i_2; i_1 a_2}^{i_1 i_2; i_1 a_2})^* & (H_{i_1 i_2; i_1 i_2}^{a_1 i_2; a_1 i_2})^* & H_{i_1 i_2; i_1 i_2}^{a_1 a_2; a_1 a_2} \end{bmatrix} \begin{bmatrix} c_{i_1 i_2}^{i_1 i_2} \\ c_{i_1 i_2}^{a_1 i_2} \\ c_{i_1 i_2}^{a_1 a_2} \end{bmatrix} = E \begin{bmatrix} c_{i_1 i_2}^{i_1 i_2} \\ c_{i_1 i_2}^{a_1 i_2} \\ c_{i_1 i_2}^{a_1 a_2} \end{bmatrix}. \quad (5.42)$$

or, in simpler notation,

$$\begin{bmatrix} E_{HF} & 0 & H_{02} \\ 0 & H_{11} & H_{12} \\ (H_{02})^* & H_{12}^* & H_{22} \end{bmatrix} \begin{bmatrix} c_{i_1 i_2}^{i_1 i_2} \\ c_{i_1 i_2}^{a_1 i_2} \\ c_{i_1 i_2}^{a_1 a_2} \end{bmatrix} = E \begin{bmatrix} c_{i_1 i_2}^{i_1 i_2} \\ c_{i_1 i_2}^{a_1 i_2} \\ c_{i_1 i_2}^{a_1 a_2} \end{bmatrix} \quad (5.43)$$

We could solve the eigenproblem directly in this case (we can write analytic solutions for anything less than a 5x5 problem), but the result is too complicated to give us much insight. To gain insight, we can approximate the solution by guessing the lowest root of the secular equation using Newton’s method. This gives

$$E_0 \approx E_{HF} + \frac{(H_{11} - E_{HF}) |H_{02}|^2}{|H_{12}|^2 + |H_{02}|^2 - (H_{11} - E_{HF})(H_{22} - E_{HF})} \quad (5.44)$$

Note that the single-excited state energy is not necessarily inconsequential: the single-excited state interacts with the doubly-excited state, which in turn interacts with the ground state through the

matrix element  $H_{02}$ . However,

$$\begin{aligned}
\Psi^{(\lambda)}(\tau) &= \langle \Phi_{HF} | \Psi(\tau) \rangle \Phi_{HF}(\tau) \\
&\quad + (\hat{I} - \hat{P})(\mathbb{E} - \hat{F})^{-1}(\mathbb{E} - E^{(\lambda)} + \lambda \hat{V}) \\
&\quad \times \left( \langle \Phi_{HF} | \Psi(\tau) \rangle \Phi_{HF}(\tau) \right. \\
&\quad \left. + (\hat{I} - \hat{P})(\mathbb{E} - \hat{F})^{-1}(\mathbb{E} - E^{(\lambda)} + \lambda \hat{V}) \right) \Psi^{(\lambda)}(\tau) \\
&= \langle \Phi_{HF} | \Psi(\tau) \rangle \Phi_{HF}(\tau) + (\hat{I} - \hat{P})(\mathbb{E} - \hat{F})^{-1} \\
&\quad \times (\mathbb{E} - E^{(\lambda)} + \lambda \hat{V}) \langle \Phi_{HF} | \Psi(\tau) \rangle \Phi_{HF}(\tau) \\
&\quad + \left[ (\hat{I} - \hat{P})(\mathbb{E} - \hat{F})^{-1}(\mathbb{E} - E^{(\lambda)} + \lambda \hat{V}) \right]^2 \Psi(\tau) \\
&= \langle \Phi_{HF} | \Psi(\tau) \rangle \sum_{n=0}^{\infty} \left[ (\hat{I} - \hat{P})(\mathbb{E} - \hat{F})^{-1}(\mathbb{E} - E^{(\lambda)} + \lambda \hat{V}) \right]^n \Phi_{HF}(\tau)
\end{aligned}$$

is usually rather small, and

so the doubly excited states are more important than the single excited states. In the limit where  $H_{12} = 0$ , then

$$E_0 = \frac{E_{HF} + H_{22}}{2} - \frac{1}{2} \sqrt{(E_{HF} - H_{22})^2 + 4|H_{02}|^2} \quad (5.45)$$

It is clear that the general CISD eigenproblem has the same form, Eq. (5.42), and will obey similar principles of solution. Unlike Hartree-Fock (cost  $\sim K^3$ ) and CIS (cost  $\sim K^4$ ), the cost of CISD increases as  $K^6$ ,<sup>23</sup> roughly proportional to the size of the system raised to the sixth power.)

## B. Multireference Singles and Doubles CI (MRSDCI or MRCISD)

As is apparent from the examples we presented, there are times where several different Slater determinants will be required to describe an ground state. For example, for the ozone molecule both the Slater determinant where the  $1a_2$  orbital is doubly occupied,  $\Phi_{1a_2} \equiv |\psi_1 \dots \psi_{1a_2} \alpha \psi_{1a_2} \beta|$ , and the Slater determinant where the  $2b_1$  orbital is doubly occupied,  $\Phi_{2b_1} \equiv |\psi_1 \dots \psi_{2b_1} \alpha \psi_{2b_1} \beta| = \Phi_{1a_2 \alpha, 1a_2 \beta}^{2b_1 \alpha, 2b_1 \beta}$  are very important. In fact, the second configuration is so important that the Hartree-Fock approximation is totally unacceptable: even a very crude model for ozone requires treating both states. Consequently, we might expect that an appropriate model for the wave function could be obtained by considering all the single and double excitations from the  $\Phi_{1a_2}$  and all the single and double excitations from  $\Phi_{2b_1}$ :

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<sup>23</sup> More accurate, the cost of CISD is proportional to  $N^2(K - N)^4$ .

$$\begin{aligned}
\Psi_{MRSDCI} \approx & c_{1a_2} \Phi_{1a_2} + \underbrace{\sum_{i=1}^N \sum_{a=N+1}^K c_i^a \Phi_i^a}_{\text{single exc. from } \Phi_{1a_2}} + \underbrace{\sum_{i>j=1}^N \sum_{a>b=N+1}^K c_{ij}^{ab} \Phi_{ij}^{ab}}_{\text{double exc. from } \Phi_{1a_2} \text{ excitations (D)}} \\
& + \underbrace{\sum_{i<1a_2}^N \sum_{a=N+1}^K c_i^a \Phi_{i,1a_2\alpha,1a_2\beta}^{a,2b_1\alpha,2b_1\beta}}_{\text{single exc. from } \Phi_{2b_1}} + \underbrace{\sum_{i_1<j<1a_2}^N \sum_{a>b=N+1}^K \Phi_{i,j,1a_2\alpha,1a_2\beta}^{a,b,2b_1\alpha,2b_1\beta}}_{\text{double exc. from } \Phi_{2b_1}}
\end{aligned} \tag{5.46}$$

Notice that because  $\Phi_{2b_1}$  is a double excitation of  $\Phi_{1a_2}$ , Equation (5.46) actually includes triple and quadruple excitations terms. However, because the triples and quadruples being considered are very special (only the types listed on the second line in Eq. (5.46)), the calculations is relatively easy—very easy compared to considering all the triple and quadruple excitations.

When you know what configurations to employ, MRSDCI is among the most accurate and efficient methods. However, it is difficult to learn which configurations should be used (one esteemed computational chemist calls it a “black art”), and there are very few people who can do so reliably. The problem is that picking out the important configurations must be done before the calculation is done, requiring a deep intuition about the system. (Many people would argue that, for instance, that occupation of the higher-energy  $7a_1$  and  $5b_2$  orbitals should also be considered, as should be the possibility that the electrons are taken from the  $6a_1$  orbital.) There are some people with such deep intuition, and there are “pretenders” (like your prof.).

The role of the different configurations in Eq. (5.46) serves to demonstrate the importance of what is often called “static” versus “dynamic” electron correlation. Static, or non-dynamic, electron correlation is due to the non-crossing rule—the “repelling” of nearly degenerate molecular states. Computing the energy using the wave function

$$\Psi \approx c_{1a_2} \Phi_{1a_2} + c_{2b_1} \Phi_{2b_1} \tag{5.47}$$

would approximate the static electron correlation energy in ozone. Similarly, one could approximate the static electron correlation in Beryllium with  $\Psi \approx c_{1s^2 2s^2} \Phi_{1s^2 2s^2} + c_{1s^2 2p^2} \Phi_{1s^2 2p^2}$ . Because the coefficient of each Slater determinant is rather large, static electron configuration affects the way electrons are distributed in important ways. For example, in the ozone atom, mixing the  $2b_1$  configuration plays a key role in reducing the unfavorable positive charge at the central oxygen atom, which has a formal charge of +1 in the  $\Phi_{1a_2}$  configuration. There is a sense, then, in which static electron correlation affects the way electrons are arranged with respect to the molecular nuclei.

“Dynamic” correlation has no clear provenance in the non-crossing rule, representing the “repulsion” due to states that are energetically far apart. There is a sense in which dynamic correlation is primarily concerned not with how electrons are arranged about the nuclei, but in how electrons “move” with respect to each other, and incorporates the detailed dependence on the interelectronic distance,  $|\mathbf{r}_i - \mathbf{r}_j|$ , that the electron-electron repulsion term in the exact Hamiltonian requires.

Based on this classification, in cases where there are “near degeneracies”, there are low-lying doubly excited states, which affect the energy a large amount.<sup>24</sup> This means that there are relatively

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<sup>24</sup> Sometimes the low-lying states do not have suitable symmetry, and do not interact with the ground state for that reason. (Recall that the non-crossing rule only applies to states with the same symmetry.) In most larger molecules, there is no symmetry, however, and low-lying orbitals always imply important static correlation effects.

important quadruple excited states, and we can include these states by moving beyond the Hartree-Fock reference system. The best, and most computationally affordable, methods are multi-reference singles and doubles CI methods, but they require choosing the appropriate state. Sometimes one uses so-called “complete active space” reference methods (CASSCF and MCSCF are two popular variants), which are very useful for including static correlation but, in general, are too costly to allow one to also include adequate dynamic correlation because “complete active space” includes a number of relatively “unimportant” configurations. The benefit of such methods, which I won’t dwell on, is that they don’t require the user to be able to “pick out” configurations. With this minor exception, however, the general rule is that:

- When static correlation is important, the Hartree-Fock description of a molecule is poor. Static correlation is *always* addressed by including a *few*, nearly degenerate, Slater determinants.
- Dynamic correlation is always important, and is more “universal”—not depending on the degeneracy or near degeneracy of the ground state. It usually takes *many* Slater determinants to address dynamic correlation—single and double excitations from the important “static-correlation” wave function, at the very least.

What happens if you, naively, perform a CISD calculation for a system like Ozone? Well, you are including both of the very important Slater determinants,  $\Phi_{1a_2}$  and  $\Phi_{2b_1}$ , and so static correlation is being accounted for. However, you are only considering single and double excitations relative to the  $\Phi_{1a_2}$  determinant, and so only this state is being “dynamically correlated.” Equivalently, because the single and double excitations from  $\Phi_{2b_1}$  were neglected, the effects of dynamic correlation on this state were neglected. We conclude, then, that a CISD calculation will obtain the static correlation and a large amount of the dynamic correlation associated with the  $\Phi_{1a_2}$  determinant, while neglecting the dynamic correlation of the  $\Phi_{2b_1}$  determinant. We may reasonably suppose, then, that the MRSDCI calculation will obtain significantly more dynamic correlation than the single-reference CISD calculation, and so when static correlation is important, the CISD wave function tends to be dramatically undercorrelated.

### C. CISD with Triple and Quadruple Excitations, CISDTQ

Observing Eq. (5.46), we recognize that what occurs in MRSDCI is that we include a few of the “important” triple and quadruple excitations. For the non-savant, it is often difficult to determine what these “important” excitations are, and so we might choose to include *all* the triple and quadruple excitations,

$$\begin{aligned} \Psi_{\text{CISDTQ}} = & c_0 \Phi_0 + \underbrace{\sum_{i=1}^N \sum_{a=N+1}^K c_i^a \Phi_i^a}_{\text{single excitations (S)}} + \underbrace{\sum_{i>j=1}^N \sum_{a>b=N+1}^K c_{ij}^{ab} \Phi_{ij}^{ab}}_{\text{double excitations (D)}} \\ & + \underbrace{\sum_{i>j>k=1}^N \sum_{a>b>c=N+1}^K c_{ijk}^{abc} \Phi_{ijk}^{abc}}_{\text{triple excitations (T)}} + \underbrace{\sum_{i>j>k>l=1}^N \sum_{a>b>c>d=N+1}^K c_{ijkl}^{abcd} \Phi_{ijkl}^{abcd}}_{\text{quadruple excitations (Q)}} \end{aligned} \quad (5.48)$$

This will include static correlations due to single and doubly excited Slater determinants and, less importantly, “higher order” dynamical correlation effects.

What are “higher-order” dynamical correlation effects? In a CISD calculation, the dynamics correlation of doubly-excited states has not been considered. That is, we have not treated the “single

and double excitations” of the doubly-excited states. Thus, when we incorporate the triple and quadruple excitations, we are both “correlating” any important “static-correlation” Slater determinants for the system and providing correlation corrections to the “dynamic correlation” Slater determinants. This sort of “second order” correlation is important, but it is a lot less important than the “first-order” dynamic correlation due to single and double excitations. In practice, the order of the importance of the various correlation terms is double excit.  $\gg$  quadruple excit.  $>$  single excit.  $\approx$  triple excit.. The next most important terms are the hexuple-excitations, which serve to correlate the quadruple excited states, which help correlate the double excited states, which correlate the ground state directly.

The above “word picture” is most clear when we consider the various sorts of matrix elements. We know that the single excitations do not affect the ground state energy directly,

$$\langle \Phi_i^a | \hat{H} | \Phi_{HF} \rangle = 0 \quad (5.49)$$

but the double excitations do.

$$\langle \Phi_{HF} | \hat{H} | \Phi_{ij}^{ab} \rangle \equiv \langle \psi_i \psi_j | \hat{v}_{ee} | \psi_a \psi_b \rangle - \langle \psi_i \psi_j | \hat{v}_{ee} | \psi_b \psi_a \rangle \quad (5.50)$$

Each term in Eq. (5.50) has the form of two distributions with zero charge interacting, for instance,

$$\langle \psi_i \psi_j | \hat{v}_{ee} | \psi_a \psi_b \rangle \equiv \delta_{\sigma_i \sigma_a} \delta_{\sigma_j \sigma_b} \iint \frac{(\psi_i^*(\mathbf{r}') \psi_a(\mathbf{r}')) (\psi_j^*(\mathbf{r}') \psi_b(\mathbf{r}'))}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \quad (5.51)$$

We expect such terms to be smaller than the interaction of a distribution with itself, and can show that:<sup>25</sup>

$$\left| \iint \frac{(\psi_i^*(\mathbf{r}) \psi_a(\mathbf{r})) (\psi_j^*(\mathbf{r}') \psi_b(\mathbf{r}'))}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \right| \leq \frac{1}{2} \left( \iint \frac{(\psi_i^*(\mathbf{r}) \psi_a(\mathbf{r})) (\psi_i^*(\mathbf{r}') \psi_a(\mathbf{r}'))}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + \iint \frac{(\psi_j^*(\mathbf{r}) \psi_b(\mathbf{r})) (\psi_j^*(\mathbf{r}') \psi_b(\mathbf{r}'))}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \right) \leq \left( \frac{K_{ia} + K_{jb}}{2} \right) \quad (5.52)$$

The “off diagonal” terms in the Hamiltonian matrix then, being a difference between two small terms, is also small.

Because the one- and two-electron integrals of Hartree products differing by more than two orbitals are all zero, triple, quadruple, and other higher-order excitations do not affect the ground state energy directly either,

$$0 = \langle \Phi_{HF} | \hat{H} | \Phi_i^a \rangle = \langle \Phi_{HF} | \hat{H} | \Phi_{ijk}^{abc} \rangle = \langle \Phi_{HF} | \hat{H} | \Phi_{ijkl}^{abcd} \rangle = \dots \quad (5.53)$$

The single excitations affect the double excitations. Using our rules for Hartree products and Slater determinates, we obtain<sup>26</sup>

$$(5.54)$$

The first and third terms can be written as an interaction energy between a distribution with charge one and a distribution with charge zero, for instance,

$$\langle \psi_a \psi_j | \hat{v}_{ee} | \psi_a \psi_b \rangle = \delta_{\sigma_j \sigma_b} \iint \frac{|\psi_a(\mathbf{r})|^2 (\psi_j^*(\mathbf{r}') \psi_b(\mathbf{r}'))}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \quad (5.55)$$

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<sup>25</sup> This is a sort of Cauchy inequality also. The key is that because  $\frac{1}{|\mathbf{r} - \mathbf{r}'|}$  is positive, we can regard

$\iint f(\mathbf{r}) \frac{1}{|\mathbf{r} - \mathbf{r}'|} f(\mathbf{r}') d\mathbf{r} d\mathbf{r}'$  as a norm, which measures the magnitude of a function. Then the Cauchy inequality

holds in the form  $2\|xy\| \leq \|x\|^2 + \|y\|^2$ , which gives Eq. (5.59).

<sup>26</sup> The derivation of Brillouin’s theorem is similar to this analysis.

and, using the Cauchy inequality (cf. Eq. (2.90))

$$\left| \psi_j^*(\mathbf{r}') \psi_b(\mathbf{r}') \right| \leq \frac{|\psi_j^*(\mathbf{r}')|^2 + |\psi_b(\mathbf{r}')|^2}{2} \quad (5.56)$$

we have that

$$\begin{aligned} \langle \psi_a \psi_j | \hat{v}_{ee} | \psi_a \psi_b \rangle &= \delta_{\sigma_j \sigma_b} \iint \frac{|\psi_a(\mathbf{r})|^2 (\psi_j^*(\mathbf{r}') \psi_b(\mathbf{r}'))}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \\ &< \delta_{\sigma_j \sigma_b} \iint \frac{|\psi_a(\mathbf{r})|^2 |\psi_j^*(\mathbf{r}') \psi_b(\mathbf{r}')|}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \\ &< \frac{\delta_{\sigma_j \sigma_b}}{2} \left( \iint \frac{|\psi_a(\mathbf{r})|^2 |\psi_j^*(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + \iint \frac{|\psi_a(\mathbf{r})|^2 |\psi_b^*(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \right) \\ &< \delta_{\sigma_j \sigma_b} \left( \frac{J_{aj} + J_{ab}}{2} \right) \end{aligned} \quad (5.57)$$

Because integrals like Eq. (5.55) represent an interaction energy between a distribution with unit charge and a distribution with zero charge, it should be unsurprising that it is always less than comparable Coulomb integrals. We also note that the first and third integrals have in Eq. (5.54) have the same form but opposite signs; some cancellation between these terms can occur.

The second and fourth terms are interaction energies between two different distributions, both with zero charge. For example,

$$\langle \psi_a \psi_j | \hat{v}_{ee} | \psi_b \psi_a \rangle \equiv \delta_{\sigma_a \sigma_b} \delta_{\sigma_j \sigma_a} \iint \frac{(\psi_a^*(\mathbf{r}) \psi_b(\mathbf{r})) (\psi_j^*(\mathbf{r}') \psi_a(\mathbf{r}'))}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \quad (5.58)$$

As per our discussion of the double excitations, the interaction of a charge distribution with itself is larger than the interaction of the charge density with another distribution, so

$$\begin{aligned} \left| \iint \frac{(\psi_a^*(\mathbf{r}) \psi_b(\mathbf{r})) (\psi_j^*(\mathbf{r}') \psi_a(\mathbf{r}'))}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \right| &\leq \frac{1}{2} \left( \iint \frac{(\psi_a^*(\mathbf{r}) \psi_b(\mathbf{r})) (\psi_a^*(\mathbf{r}') \psi_b(\mathbf{r}'))}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + \iint \frac{(\psi_j^*(\mathbf{r}) \psi_a(\mathbf{r})) (\psi_j^*(\mathbf{r}') \psi_a(\mathbf{r}'))}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \right) \\ &\leq \left( \frac{K_{ab} + K_{aj}}{2} \right) \end{aligned} \quad (5.59)$$

In any event, we are led to conclude that the coupling between singly and doubly excited determinants is weak.

The matrix element between single and triple excitations is similar to the matrix element between the Hartree-Fock wave function and the doubles, as is the matrix element between double and quadruple excitations:

$$\begin{aligned} \langle \Phi_i^a | \hat{H} | \Phi_{ijk}^{abc} \rangle &= \langle \psi_j \psi_k | \hat{v}_{ee} | \psi_b \psi_c \rangle - \langle \psi_j \psi_k | \hat{v}_{ee} | \psi_c \psi_b \rangle \\ \langle \Phi_{ij}^{ab} | \hat{H} | \Phi_{ijkl}^{abcd} \rangle &= \langle \psi_k \psi_l | \hat{v}_{ee} | \psi_c \psi_d \rangle - \langle \psi_k \psi_l | \hat{v}_{ee} | \psi_d \psi_c \rangle. \end{aligned} \quad (5.60)$$

Similarly, the size of the matrix elements coupling double and triple excitations and triple and quadruple excitations will resemble the interaction between the single and double excitations (but the form is bit more complicated). In the end, the Hamiltonian matrix for which the eigenvalue problem needs to be solved can be written

$$\begin{bmatrix}
E_{HF} & 0 & \langle \Phi_0 | \hat{H} | \Phi_{ij}^{ab} \rangle & 0 & 0 & 0 & \dots \\
0 & \langle \Phi_0 | \hat{H} | \Phi_i^a \rangle & \langle \Phi_i^a | \hat{H} | \Phi_{ij}^{ab} \rangle & \langle \Phi_i^a | \hat{H} | \Phi_{ijk}^{abc} \rangle & 0 & 0 & \dots \\
\langle \Phi_0 | \hat{H} | \Phi_{ij}^{ab} \rangle^* & \langle \Phi_i^a | \hat{H} | \Phi_{ij}^{ab} \rangle^* & \langle \Phi_{ij}^{ab} | \hat{H} | \Phi_{ij}^{ab} \rangle & \langle \Phi_{ij}^{ab} | \hat{H} | \Phi_{ijk}^{abc} \rangle & \langle \Phi_{ij}^{ab} | \hat{H} | \Phi_{ijkl}^{abcd} \rangle & 0 & \dots \\
0 & \langle \Phi_i^a | \hat{H} | \Phi_{ijk}^{abc} \rangle^* & \langle \Phi_{ij}^{ab} | \hat{H} | \Phi_{ijk}^{abc} \rangle^* & \langle \Phi_{ijk}^{abc} | \hat{H} | \Phi_{ijk}^{abc} \rangle & \langle \Phi_{ijk}^{abc} | \hat{H} | \Phi_{ijkl}^{abcd} \rangle & \langle \Phi_{ijk}^{abc} | \hat{H} | \Phi_{ijklm}^{abcde} \rangle & \\
0 & 0 & \langle \Phi_{ij}^{ab} | \hat{H} | \Phi_{ijkl}^{abcd} \rangle^* & \langle \Phi_{ijk}^{abc} | \hat{H} | \Phi_{ijkl}^{abcd} \rangle^* & \langle \Phi_{ijkl}^{abcd} | \hat{H} | \Phi_{ijkl}^{abcd} \rangle & \langle \Phi_{ijkl}^{abcd} | \hat{H} | \Phi_{ijklm}^{abcde} \rangle & \\
0 & 0 & 0 & \langle \Phi_{ijk}^{abc} | \hat{H} | \Phi_{ijklm}^{abcde} \rangle^* & \langle \Phi_{ijkl}^{abcd} | \hat{H} | \Phi_{ijklm}^{abcde} \rangle^* & \langle \Phi_{ijklm}^{abcde} | \hat{H} | \Phi_{ijklm}^{abcde} \rangle & \\
\vdots & \vdots & \vdots & & & & \ddots
\end{bmatrix}
\quad (5.61)$$

Equation (5.61) is the foundation for our preceding discussion: quadruple excitations are important because they make the same sorts of corrections to doubly-excited determinants that the doubly-excited determinants make to the Hartree-Fock wave function. Singly and triply excited determinants are also important (but marginally less so). Higher-order excitations are less important: for example, sixth-order corrections correct the quadruply excited determinants, which corrects the doubly excited determinants, which corrects the ground state wave function: this gives a correction to a correction. For most systems with rather few electrons, these higher excitation levels are not that important. (The corrections are more important for systems with more electrons but, for systems with many electrons, it becomes impossible to perform such accurate calculations, so this is a moot point.)

How expensive is a CISDTQ calculation? A CISDTQ calculations cost is proportional to  $K^{10}$ .<sup>27</sup> This is practically impossible for anything except a small molecule, which is why there is so much interest in multi-reference methods.

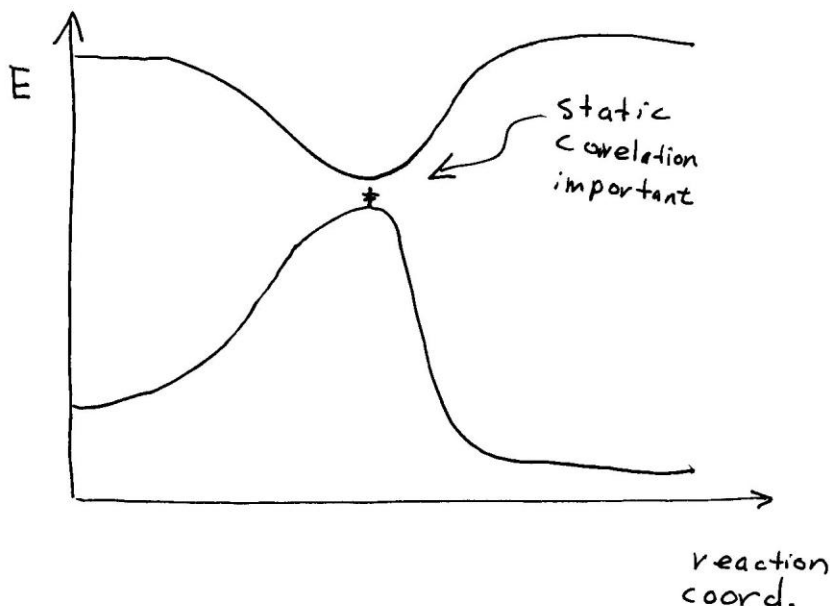
## D. Describing “chemistry” with Configuration Interaction

Configuration Interaction calculations can be particularly problematic when we try to consider chemical processes. The first problem is again the problem of static correlation: even if there is only one important configuration near the equilibrium geometry, for different molecular geometries there will often be additional important states. A simple and important case occurs near the transition state in many chemical reactions, wherein the gap between the ground and first excited state is often small. Because static correlation will be important, some quadruple excitations are needed to describe the “reaction path.” For example, for Cope rearrangements that occur via a diyl intermediate, there are two important configurations at for this intermediate, but only one important configuration when the molecule resembles either reactants or products. Describing such reactions, then, requires (at minimum) either CISDTQ or MRSDCI. You can imagine how frustrating it is to try to find the reference determinants for describing chemical processes: one must identify not only the important determinants in the reactant and product state, but also include such determinants as are necessary to describe the static correlation of intermediates and transition states. Moreover, one must identify these states at the beginning of one’s theoretical treatment. In particular, when the purpose of a calculation is to fill gaps in experimental knowledge, it seems unlikely that you will be able to, with

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<sup>27</sup> More precisely and generally, the cost of a configuration interaction calculation including all excited state determinants with 1,2,3,... $k$  excitations is  $\text{cost} \sim (N)^k (K - N)^{k+2}$ .

any certainty, select the correct reference configurations. You will need to be lucky or good, or otherwise use a treatment with quadruple excitations.



**Figure:** Static Correlation can be important near transitions states, which are often associated with “avoided crossings” of potential energy curves.

Molecular dissociation processes are particularly problematic for two reasons. First of all, static correlation effects can be important as bonds are stretched, since bonding and anti-bonding orbitals tend to approach each others energy as the bond length increases.

Second, there is the problem of *size consistency*. A computational method is said to be size consistent if it predicts that the energy of two atoms or molecules,  $A$  and  $B$ , that are infinitely far apart is the same as the sum of the energies of the isolated systems,

$$\lim_{R \rightarrow \infty} E \left( \begin{matrix} A-B \\ R \end{matrix} \right) = E(A) + E(B) \quad (5.62)$$

Configuration interaction calculations (except for Full-CI) are not size consistent. For example, consider a CISD calculation on the Helium dimer ( $A = B = \text{He}$  in Eq. (5.62)). Since Helium has only two electrons, the energy of the Helium atom is computed exactly by an CISD calculation, which amounts to Full-CI for this system. However, for two Helium atoms very far apart, Full-CI requires a CISDTQ calculation, and the CISD calculation does not allow configurations where both Helium atoms are simultaneously in an excited state. More explicitly, let  $1_l$  denote the  $\alpha$ -spin 1s-orbital on the “left” Helium atom and  $\bar{1}_l$  denote the  $\beta$ -spin 1s-orbital for the left Helium atom, with similar notation for the “right” atom and also the 2s orbital. We ignore higher excitations. The wave function for the “left hand” Helium atom has four configurations:

$$\Psi_{\text{He}}(\mathbf{z}_1, \mathbf{z}_2) = c_{1_l \bar{1}_l} \Phi_{1_l \bar{1}_l}^{1_l \bar{1}_l} + c_{1_l \bar{2}_l} \Phi_{1_l \bar{2}_l}^{2_l \bar{1}_l} + c_{1_l \bar{1}_l} \Phi_{1_l \bar{1}_l}^{1_l \bar{2}_l} + c_{1_l \bar{2}_l} \Phi_{1_l \bar{2}_l}^{2_l \bar{2}_l} \quad (5.63)$$

and the wave function for the Helium dimer has



$$\begin{aligned}
\Psi_{He-He}(\mathbf{z}_1, \mathbf{z}_2, \mathbf{z}_3, \mathbf{z}_4) = & c_{l_l \bar{l}_l l_r \bar{l}_r} \Phi_{l_l \bar{l}_l l_r \bar{l}_r} + c_{l_l \bar{l}_l l_r \bar{l}_r} \Phi_{l_l \bar{l}_l l_r \bar{l}_r}^{2_l \bar{2}_l} + c_{l_l \bar{l}_l l_r \bar{l}_r} \Phi_{l_l \bar{l}_l l_r \bar{l}_r}^{1_l \bar{2}_l 1_r \bar{2}_r} + c_{l_l \bar{l}_l l_r \bar{l}_r} \Phi_{l_l \bar{l}_l l_r \bar{l}_r}^{1_l \bar{2}_l 2_r \bar{2}_r} \\
& + c_{l_l \bar{l}_l l_r \bar{l}_r} \Phi_{l_l \bar{l}_l l_r \bar{l}_r}^{1_l \bar{2}_l 1_r \bar{2}_r} + c_{l_l \bar{l}_l l_r \bar{l}_r} \Phi_{l_l \bar{l}_l l_r \bar{l}_r}^{2_l \bar{2}_l 1_r \bar{2}_r} + c_{l_l \bar{l}_l l_r \bar{l}_r} \Phi_{l_l \bar{l}_l l_r \bar{l}_r}^{2_l \bar{2}_l 2_r \bar{2}_r} + c_{l_l \bar{l}_l l_r \bar{l}_r} \Phi_{l_l \bar{l}_l l_r \bar{l}_r}^{2_l \bar{2}_l 1_r \bar{2}_r} \\
& + c_{l_l \bar{l}_l l_r \bar{l}_r} \Phi_{l_l \bar{l}_l l_r \bar{l}_r}^{1_l \bar{2}_l 2_r \bar{2}_r} + c_{l_l \bar{l}_l l_r \bar{l}_r} \Phi_{l_l \bar{l}_l l_r \bar{l}_r}^{1_l \bar{2}_l 1_r \bar{2}_r} + c_{l_l \bar{l}_l l_r \bar{l}_r} \Phi_{l_l \bar{l}_l l_r \bar{l}_r}^{1_l \bar{2}_l 2_r \bar{2}_r}
\end{aligned} \quad (5.64)$$

However, the exact wave function for two separated Helium atoms (so that the correlation between the electrons in the right-side and left-side atoms is small) is

$$\Psi_{He_l+He_r}(\mathbf{z}_1, \mathbf{z}_2, \mathbf{z}_3, \mathbf{z}_4) = \mathcal{A} \left[ \begin{aligned} & \left( c_{l_l \bar{l}_l} \Phi_{l_l \bar{l}_l} + c_{l_l \bar{l}_l} \Phi_{l_l \bar{l}_l}^{2_l \bar{2}_l} + c_{l_l \bar{l}_l} \Phi_{l_l \bar{l}_l}^{1_l \bar{2}_l} + c_{l_l \bar{l}_l} \Phi_{l_l \bar{l}_l}^{2_l \bar{2}_l} \right) \\ & \times \left( c_{l_r \bar{l}_r} \Phi_{l_r \bar{l}_r} + c_{l_r \bar{l}_r} \Phi_{l_r \bar{l}_r}^{2_r \bar{2}_r} + c_{l_r \bar{l}_r} \Phi_{l_r \bar{l}_r}^{1_r \bar{2}_r} + c_{l_r \bar{l}_r} \Phi_{l_r \bar{l}_r}^{2_r \bar{2}_r} \right) \end{aligned} \right] \quad (5.65)$$

where  $\mathcal{A}\Phi_l\Phi_r$  denotes the antisymmetric product of the wave functions for the left- and right-side atoms. However, Eq. (5.65) will include terms contain four excitations, which are not in Eq. (5.64), and so the energy of the two separated Helium atoms (from the wave function in Eq. (5.64)) is greater than the sum of the energies of the two Helium atoms (from the wave function in Eq. (5.65)).

The same argument can clearly be made for any dissociating system: the “dissociated” molecule is described less accurately than its fragments alone, so that, for anything less than Full-CI,

$$\lim_{R \rightarrow \infty} E \left( \begin{array}{c} \text{A-B} \\ \text{R} \end{array} \right) > E(\text{A}) + E(\text{B}). \quad (5.66)$$

For small molecules, the size consistency error is often approximately removed using the “Davidson correction” formula,

$$E = E_{CISD} + (1 - c_0^2)(E_{CISD} - E_{HF}), \quad (5.67)$$

where  $E_{CISD}$  is the energy from the CISD calculation,  $E_{HF}$  is the energy from the Hartree-Fock calculation, and  $c_0$  is the coefficient of the Hartree-Fock Slater determinant in the CISD wave function, cf. Eq. (5.24). For MRSDCI and CISDTQ calculations, the size-consistency error

$$\mathcal{E}_{\text{size consistency}} \equiv \left( \lim_{R \rightarrow \infty} E \left( \begin{array}{c} \text{A-B} \\ \text{R} \end{array} \right) \right) - E(\text{A}) + E(\text{B}) \quad (5.68)$$

is often smaller than the error in the correlation energy, and so the error in the description of molecular dissociation is primarily due to the imperfect treatment of dynamical correlation, not the problem of size consistency.

As a general rule, I prefer not to use configuration interaction calculations when describing molecular dissociation and association reactions.

## E. Interpretation of Configuration-Interaction Calculations

People often ask what a wave function with the form of Eq. (5.24),

$$\begin{aligned}
\Psi = & c_0 \Phi_0 + \underbrace{\sum_{i=1}^N \sum_{a=N+1}^K c_i^a \Phi_i^a}_{\text{single excitations (S)}} + \underbrace{\sum_{i>j=1}^N \sum_{a>b=N+1}^K c_{ij}^{ab} \Phi_{ij}^{ab}}_{\text{double excitations (D)}} \\
& + \underbrace{\sum_{i>j>k=1}^N \sum_{a>b>c=N+1}^K c_{ijk}^{abc} \Phi_{ijk}^{abc}}_{\text{triple excitations (T)}} + \underbrace{\sum_{i>j>k>l=1}^N \sum_{a>b>c>d=N+1}^K c_{ijkl}^{abcd} \Phi_{ijkl}^{abcd}}_{\text{quadruple excitations (Q)}} + \dots
\end{aligned} \quad (5.69)$$

has to do with electron correlation. After all, the problem with the Hartree-Fock theory that the intricate and detailed collective motions of the electrons induced by the electron-electron repulsion term were “averaged over”, so that the electrons move essentially independently. Why does adding excited-state determinants help? Some insight can be gleaned from analysis like that in problem VI of homework set 3, but a hand-waving argument may be instructive.

- The Single excitation,  $\Phi_i^a$  represents “moving one electron from orbital  $\psi_i(\mathbf{z})$  to orbital  $\psi_j(\mathbf{z})$ ”, while all the other electrons are “left alone.” So we are moving one electron, at a time, independently and, if you like to think in “real space”, you can think of this as describing how the wave function changes as we move an electron from a place,  $\mathbf{r}$ , where  $\psi_i(\mathbf{r})$  is large to a place,  $\mathbf{r}'$ , where  $\psi_a(\mathbf{r}')$  is large. However, we are only moving one electron at a time—we are moving electrons “independently.” But this is the essence of the Hartree-Fock approximation: “move electrons independently.” We expect, then, that the single excitations do not correct the Hartree-Fock energy. This is Brillouin’s theorem.
- The double excitation,  $\Phi_{ij}^{ab}$ , describes two electrons moving together. One electron, with spin and position  $\mathbf{z}_\alpha$ , moves from the state described by the orbital  $\psi_i(\mathbf{z}_\alpha)$  to the state described by the orbital  $\psi_a(\mathbf{z}_\alpha)$ , at the same time that another electron, with spin and position  $\mathbf{z}_\beta$ , moves from  $\psi_j(\mathbf{z}_\beta)$  to  $\psi_b(\mathbf{z}_\beta)$ . Double excitations describe the way two electrons move together or, if you like, the “correlation” between two different electrons’ motions.
- The triple excitation,  $\Phi_{ijk}^{abc}$ , describes three electrons, with coordinates  $\mathbf{z}_\alpha, \mathbf{z}_\beta, \mathbf{z}_\gamma$ , moving together. One electron moves from  $\psi_i(\mathbf{z}_\alpha)$  to  $\psi_a(\mathbf{z}_\alpha)$ , another electron moves from  $\psi_j(\mathbf{z}_\beta)$  to  $\psi_b(\mathbf{z}_\beta)$ , and a third electron moves from  $\psi_k(\mathbf{z}_\gamma)$  to  $\psi_c(\mathbf{z}_\gamma)$ . So triple excitations describe “three body correlations.”
- The quadruple excitation,  $\Phi_{ijkl}^{abcd}$ , describes four electrons, with coordinates  $\mathbf{z}_\alpha, \mathbf{z}_\beta, \mathbf{z}_\gamma, \mathbf{z}_\delta$ , moving together. One electron moves from  $\psi_i(\mathbf{z}_\alpha)$  to  $\psi_a(\mathbf{z}_\alpha)$ , another electron moves from  $\psi_j(\mathbf{z}_\beta)$  to  $\psi_b(\mathbf{z}_\beta)$ , a third electron moves from  $\psi_k(\mathbf{z}_\gamma)$  to  $\psi_c(\mathbf{z}_\gamma)$ , and the fourth electron moves from  $\psi_l(\mathbf{z}_\delta)$  to  $\psi_d(\mathbf{z}_\delta)$ . So quadruple excitations describe “four-electron correlations”.

## F. The conventional approach to the Coupled-Cluster Idea

(I’ll fill this in later if I get a chance—it is for your edification and so you can see the link between Couple-Cluster theory and Configuration Interaction. You wouldn’t be tested on this material.)

### III. Perturbation Theory

Since we have already explored the Hartree-Fock Hamiltonian, and since the Hartree-Fock method is rather easy computationally, we might like to use perturbation theory and, in particular, use  $\hat{F}$  to approximate the exact Hamiltonian,

$$\hat{H} = \sum_{i=1}^N -\frac{\nabla_i^2}{2} + v(\mathbf{r}_i) + \sum_{i=1}^{N-1} \sum_{j=i+1}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (5.70)$$

for which we cannot solve the Schrödinger equation. Writing the exact Hamiltonian as

$$\begin{aligned} \hat{H}^{(\lambda)} &\equiv \hat{F} + \lambda(\hat{H} - \hat{F}) \\ &= \hat{F} + \lambda\hat{V} \end{aligned} \quad (5.71)$$

(the “real” system is where  $\lambda = 1$ ), we could develop perturbation theory in the usual way, by writing the energy and the wave function as a Taylor series in  $\lambda$

$$E^{(\lambda)} \equiv E^{(0)} + \lambda \left. \frac{\partial E^{(\lambda)}}{\partial \lambda} \right|_{\lambda=0} + \frac{\lambda^2}{2!} \left. \frac{\partial^2 E^{(\lambda)}}{\partial \lambda^2} \right|_{\lambda=0} + \dots \quad (5.72)$$

$$\Psi^{(\lambda)} \equiv \Psi^{(0)} + \lambda \left. \frac{\partial \Psi^{(\lambda)}}{\partial \lambda} \right|_{\lambda=0} + \frac{\lambda^2}{2!} \left. \frac{\partial^2 \Psi^{(\lambda)}}{\partial \lambda^2} \right|_{\lambda=0} + \dots \quad (5.73)$$

This is, however, not the most convenient method in the present context, mostly because the perturbation operator,  $\hat{V} \equiv (\hat{H} - \hat{F})$ , is quite complicated.

To construct the perturbation expansion, we first define the projection operator,

$$\hat{P}\Psi(\tau) = \langle \Phi_{HF} | \Psi(\tau) \rangle \Phi_{HF}(\tau), \quad (5.74)$$

which serves to “extract” the Hartree-Fock part of the exact wave function. Using the projection operator and the identity operator,  $\hat{I}$ , we have that

$$\begin{aligned} \hat{I}\Psi(\tau) - \hat{P}\Psi(\tau) &= \Psi(\tau) - \langle \Phi_{HF} | \Psi(\tau) \rangle \Phi_{HF}(\tau) \\ (\hat{I} - \hat{P})\Psi(\tau) &= \Psi(\tau) - \langle \Phi_{HF} | \Psi(\tau) \rangle \Phi_{HF}(\tau) \\ \Psi(\tau) &= \langle \Phi_{HF} | \Psi(\tau) \rangle \Phi_{HF}(\tau) + (\hat{I} - \hat{P})\Psi(\tau) \end{aligned} \quad (5.75)$$

$(\hat{I} - \hat{P})$  is also a “projection” operator then, but it projects out of the exact wave function the portion that is *not* the Hartree-Fock wave function.

Next, we write the Schrödinger equation,

$$\begin{aligned} \hat{H}^{(\lambda)}\Psi^{(\lambda)}(\tau) &= E^{(\lambda)}\Psi^{(\lambda)}(\tau) \\ (\hat{F} + \lambda\hat{V})\Psi^{(\lambda)}(\tau) &= E^{(\lambda)}\Psi^{(\lambda)}(\tau) \\ (\mathbb{E} - \hat{F} - \lambda\hat{V})\Psi^{(\lambda)}(\tau) &= (\mathbb{E} - E^{(\lambda)})\Psi^{(\lambda)}(\tau) \\ (\mathbb{E} - \hat{F})\Psi^{(\lambda)}(\tau) &= (\mathbb{E} - E^{(\lambda)} + \lambda\hat{V})\Psi^{(\lambda)}(\tau) \\ \Psi^{(\lambda)}(\tau) &= (\mathbb{E} - \hat{F})^{-1} (\mathbb{E} - E^{(\lambda)} + \lambda\hat{V})\Psi^{(\lambda)}(\tau), \end{aligned} \quad (5.76)$$

where  $(\mathbb{E} - \hat{F})^{-1}$  denotes the inverse of the  $(\mathbb{E} - \hat{F})$  operator.

Next, we use Eq. (5.75) to obtain

$$\begin{aligned}
(\hat{I} - \hat{P})\Psi^{(\lambda)}(\tau) &= (\hat{I} - \hat{P})(\mathbb{E} - \hat{F})^{-1}(\mathbb{E} - E^{(\lambda)} + \lambda\hat{V})\Psi^{(\lambda)}(\tau) \\
\Psi^{(\lambda)}(\tau) - \langle \Phi_{HF} | \Psi(\tau) \rangle \Phi_{HF}(\tau) &= (\hat{I} - \hat{P})(\mathbb{E} - \hat{F})^{-1}(\mathbb{E} - E^{(\lambda)} + \lambda\hat{V})\Psi^{(\lambda)}(\tau) \\
\Psi^{(\lambda)}(\tau) &= \langle \Phi_{HF} | \Psi(\tau) \rangle \Phi_{HF}(\tau) + (\hat{I} - \hat{P})(\mathbb{E} - \hat{F})^{-1}(\mathbb{E} - E^{(\lambda)} + \lambda\hat{V})\Psi^{(\lambda)}(\tau)
\end{aligned} \tag{5.77}$$

If we substitute Eq. (5.77) back into itself, we obtain

$$\begin{aligned}
\Psi^{(\lambda)}(\tau) &= \langle \Phi_{HF} | \Psi(\tau) \rangle \Phi_{HF}(\tau) \\
&\quad + (\hat{I} - \hat{P})(\mathbb{E} - \hat{F})^{-1}(\mathbb{E} - E^{(\lambda)} + \lambda\hat{V}) \\
&\quad \times \left[ \langle \Phi_{HF} | \Psi(\tau) \rangle \Phi_{HF}(\tau) \right. \\
&\quad \left. + (\hat{I} - \hat{P})(\mathbb{E} - \hat{F})^{-1}(\mathbb{E} - E^{(\lambda)} + \lambda\hat{V}) \right] \Psi^{(\lambda)}(\tau) \\
&= \langle \Phi_{HF} | \Psi(\tau) \rangle \Phi_{HF}(\tau) + (\hat{I} - \hat{P})(\mathbb{E} - \hat{F})^{-1} \\
&\quad \times (\mathbb{E} - E^{(\lambda)} + \lambda\hat{V}) \langle \Phi_{HF} | \Psi(\tau) \rangle \Phi_{HF}(\tau) \\
&\quad + \left[ (\hat{I} - \hat{P})(\mathbb{E} - \hat{F})^{-1}(\mathbb{E} - E^{(\lambda)} + \lambda\hat{V}) \right]^2 \Psi(\tau) \\
&= \langle \Phi_{HF} | \Psi(\tau) \rangle \sum_{n=0}^{\infty} \left[ (\hat{I} - \hat{P})(\mathbb{E} - \hat{F})^{-1}(\mathbb{E} - E^{(\lambda)} + \lambda\hat{V}) \right]^n \Phi_{HF}(\tau)
\end{aligned} \tag{5.78}$$

The last line follows, in the same fashion, from repeated substitutions. One usually adopts the convention of *intermediate normalization*, wherein

$$\langle \Phi_{HF} | \Psi(\tau) \rangle \equiv 1. \tag{5.79}$$

With this convention, one has that

$$\Psi^{(\lambda)}(\tau) = \sum_{n=0}^{\infty} \left[ (\hat{I} - \hat{P})(\mathbb{E} - \hat{F})^{-1}(\mathbb{E} - E^{(\lambda)} + \lambda\hat{V}) \right]^n \Phi_{HF}(\tau) \tag{5.80}$$

With the convention of intermediate normalization, there is a very useful formula for  $E^{(\lambda)}$ . Namely, taking the Schrödinger equation, (5.76), and multiplying on both sides with  $\Phi_{HF}$ , we have

$$\begin{aligned}
\langle \Phi_{HF} | \hat{H}^{(\lambda)} | \Psi^{(\lambda)} \rangle &= \langle \Phi_{HF} | \mathbb{E}^{(\lambda)} | \Psi^{(\lambda)} \rangle \\
\langle \Phi_{HF} | \hat{F} + \lambda\hat{V} | \Psi^{(\lambda)} \rangle &= E^{(\lambda)} \langle \Phi_{HF} | \Psi^{(\lambda)} \rangle \\
\langle \Phi_{HF} | \hat{F} | \Psi^{(\lambda)} \rangle + \lambda \langle \Phi_{HF} | \hat{V} | \Psi^{(\lambda)} \rangle &= E^{(\lambda)} \\
\langle \hat{F} \Phi_{HF} | \Psi^{(\lambda)} \rangle + \lambda \langle \Phi_{HF} | \hat{V} | \Psi^{(\lambda)} \rangle &= E^{(\lambda)} \\
\mathcal{E}_0 \langle \Phi_{HF} | \Psi^{(\lambda)} \rangle + \lambda \langle \Phi_{HF} | \hat{V} | \Psi^{(\lambda)} \rangle &= E^{(\lambda)} \\
E^{(\lambda)} - \mathcal{E}_0 &= \lambda \langle \Phi_{HF} | \hat{V} | \Psi^{(\lambda)} \rangle
\end{aligned} \tag{5.81}$$

In Eq. (5.81), we define

$$\mathcal{E}_0 = \sum_{i=1}^N \varepsilon_i \quad (5.82)$$

and recall, from Eq. (5.16), that  $\hat{F}\Phi_{HF} = \left(\sum_{i=1}^N \varepsilon_i\right)\Phi_{HF}$ .

Note that there is an intimate connection between many-body perturbation theory and the many-electron Green's function: the identity (cf. Eq. (4.11))

$$(E - \hat{H}(\tau))G(\tau, \tau'; E) = \delta(\tau - \tau') \quad (5.83)$$

implies that  $G(\tau, \tau'; E) = (E - \hat{H})^{-1}$ , and so  $(\mathbb{E} - \hat{F})^{-1}$  can be considered to be a Green's function-type operator. Note that we have full freedom to choose  $\mathbb{E}$ , and we should do so in a way that makes the perturbation series have desirable properties.

We are, of course, primarily interested in the case where  $\lambda = 1$ . We can choose  $\mathbb{E}$  to be anything that is convenient. A particularly simple choice is Brillouin-Wigner perturbation theory, wherein  $\mathbb{E} \equiv E^{(\lambda=1)} = E$ . In this case we have to solve the simultaneous equations for the wave function and the energy,

$$\begin{aligned} \Psi(\tau) &= \sum_{n=0}^{\infty} \left( \left[ (\hat{I} - \hat{P})(E - \hat{F})^{-1} \hat{V} \right]^n \Phi_{HF}(\tau) \right) \\ E_{BW} &\equiv \frac{\langle \Psi | \hat{F} + \hat{V} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \\ &= \mathcal{E}_0 + \langle \Phi_{HF} | \hat{V} | \Psi \rangle \end{aligned} \quad (5.84)$$

The second form for the energy is based on Eq. (5.81). Brillouin-Wigner perturbation theory is rarely used in for chemical computations. (In Eq. (5.84), we have opted to omit the superscript specifying the value of  $\lambda$  whenever  $\lambda = 1$ .)

The “usual” case is called Moller-Plesset (MP) or Many-Body Perturbation Theory (MBPT). Moller-Plesset/Many-Body Perturbation Theory is a special case of the Raleigh-Schrödinger perturbation theory, wherein  $\mathbb{E}$  is chosen to be the energy of the zeroth order Hamiltonian. In this case, then, from Eq. (5.16), we have that

$$\mathbb{E}_{MBPT} \equiv \mathcal{E}_0 = \sum_{i=1}^N \varepsilon_i. \quad (5.85)$$

With Eq. (5.85), we can derive the “usual” perturbation series from the analogues of the perturbation equations in the Brillouin-Wigner case (Eq. (5.84)), namely,

$$\begin{aligned} \Psi(\tau) &= \sum_{n=0}^{\infty} \left[ (\hat{I} - \hat{P})(\mathcal{E}_0 - \hat{F})^{-1} (\mathcal{E}_0 - E + \hat{V}) \right]^n \Phi_{HF}(\tau) \\ E_{MBPT} &= \frac{\langle \Psi | \hat{F} + \hat{V} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \\ &= \mathcal{E}_0 + \langle \Phi_{HF} | \hat{V} | \Psi \rangle. \end{aligned} \quad (5.86)$$

In practice, of course, it is impossible evaluate the infinite sum in Eq. (5.86). Truncating the sum at some order,  $\kappa$ , the wave function and energy using:<sup>28</sup>

$$\begin{aligned}\Psi^{(\kappa)}(\tau) &= \sum_{n=0}^{\kappa} \left[ (\hat{I} - \hat{P}) (\mathcal{E}_0 - \hat{F})^{-1} (\mathcal{E}_0 - E + \hat{V}) \right]^n \Phi_{HF}(\tau) \\ E_{MBPT}^{(\kappa+1)} &= \mathcal{E}_0 + \langle \Phi_{HF} | \hat{V} | \Psi^{(\kappa)} \rangle.\end{aligned}\tag{5.87}$$

Because the wave function depends on the perturbation operator,  $\hat{V}$ , through terms of order  $\hat{V}^0, \hat{V}^1, \dots, \hat{V}^{(\kappa)}$ ,  $\Psi^{(\kappa)}$  is the  $\kappa^{th}$  order wave function. Note that the energy, however, is expressed as a sum of terms wherein the perturbation operator occurs to the  $0^{th}, 1^{st}, \dots, (\kappa+1)^{th}$  powers;  $E^{(\kappa+1)}$  is the  $(\kappa+1)^{th}$  order wave function. *When we truncate the perturbation expansion for the wave function at order  $\kappa-1$  and compute  $E^{(\kappa)}$ , we say we are performing  $\kappa^{th}$ -order many-body perturbation theory, which we denote  $MP\kappa$  (Moller-Plesset- $\kappa$ ) or  $MBPT\kappa$  (Many-Body-Perturbation-Theory- $\kappa$ ).*

By far the most important case is second-order perturbation theory, and I will sketch this specific case in more detail, both to present some idea of the methods involved in evaluating the sum in Eq. (5.87) and to convince you that this approach, though different from the sort of perturbation expansion technique you are used to, does in fact give the “conventional” perturbation series for the energy.

In computing  $\Psi^{(\kappa)}$  we have to evaluate how various operators act on the Hartree-Fock Hamiltonian. A key result is:

$$\begin{aligned}\hat{Q}(\tau) \Phi_{HF}(\tau) &= \int \delta(\tau - \tau') \hat{Q}(\tau') \Phi_{HF}(\tau') d\tau' \\ &= \int \left( \sum_{k=0}^{\infty} \Phi_k^*(\tau') \Phi_k(\tau) \right) \hat{Q}(\tau') \Phi_{HF}(\tau') d\tau' \\ &= \sum_{k=0}^N \Phi_k(\tau) \langle \Phi_k | \hat{Q} | \Phi_{HF} \rangle \\ &= \sum_{k=0}^N \Phi_k(\tau) \langle \Phi_k | \hat{Q} | \Phi_0 \rangle\end{aligned}\tag{5.88}$$

In the derivation of Eq. (5.88), we have denoted the set of all eigenfunctions of the zeroth-order Hamiltonian,  $\hat{F}$ , as  $\{\Phi_k\}_{k=0}^{\infty}$  with  $\Phi_0 = \Phi_{HF}$  being the Hartree-Fock wave function.<sup>29</sup> Remember that  $\{\Phi_k\}$  is the set of all Slater determinants of the Hartree-Fock orbitals, and is a complete set, as per the discussion surrounding Eq. (5.16).

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<sup>28</sup> Based on Eq. (5.87), you might suppose that you must compute the  $\kappa^{th}$  order wave function in order to obtain the  $(\kappa+1)^{st}$ -order energy. This is not true. In fact, we can compute the  $(2\kappa+1)^{st}$ -order energy,  $E^{(2\kappa+1)}$  from the  $\kappa^{th}$ -order wave function. For this reason, the “biggest difference” occurs every time you have to compute a new “improvement” to the wave function because, as we shall see in Eq. (5.101), it is only when you refine the wave function that new, higher-level, excitations enter into the energy expression. For this reason, we usually use  $\kappa=2$  (requires  $\Psi^{(1)}$ ),  $\kappa=4$  (requires  $\Psi^{(2)}$ ),  $\kappa=6$  (requires  $\Psi^{(3)}$ ), etc..

<sup>29</sup> Almost always the Hartree-Fock wave function for a ground state is chosen here. But this need not necessarily be the case.

To draw the connect to configuration interaction methods, remember that we can write all the excited state Slater determinants as single, double, triple . . . excitations of the original Slater determinant. Thus

$$\Phi_k \rightarrow \Phi_{\mathbf{i}}^{\mathbf{a}} \equiv \Phi_{i_1 i_2 \dots i_N}^{a_1 a_2 \dots a_N} \quad (5.89)$$

where  $i_1, i_2, \dots, i_N$  are the occupied orbitals of the system and  $a_1, a_2, \dots, a_N$  are any orbitals. If  $a_i = i_i$ , that indicates than no electrons are excited, and so we could rewrite the ground state Slater determinant as  $\Phi_{\mathbf{i}}^{\mathbf{i}}$ . That is we restrict ourselves to the ground state Slater determinant forcing  $i_1 = a_1, i_2 = a_2 \dots i_N = a_N$  or, in mathematical language, by requiring that

$$\delta_{\mathbf{ia}} = \prod_{k=1}^N \delta_{i_k a_k} = 1 \quad (5.90)$$

We denote the zeroth-order energy of  $\Phi_{\mathbf{i}}^{\mathbf{a}}$  as

$$\mathcal{E}_{\mathbf{i}}^{\mathbf{a}} = \sum_{k=1}^N \mathcal{E}_k + \sum_{k=1}^N (\mathcal{E}_{a_k} - \mathcal{E}_{i_k}), \quad (5.91)$$

which is just the sum of the energies of the occupied orbitals in  $\Phi_{\mathbf{i}}^{\mathbf{a}}$ ; recall Eq. (5.16). Recall that if  $f(\hat{F})$  is a function of  $\hat{F}$ , then

$$f(\hat{F})\Phi_{\mathbf{i}}^{\mathbf{a}} = f(\mathcal{E}_{\mathbf{i}}^{\mathbf{a}})\Phi_{\mathbf{i}}^{\mathbf{a}}. \quad (5.92)$$

Using Eqs. (5.88) and Eq. (5.92) repeatedly, we can now evaluate

$$\begin{aligned} \Psi^{(1)}(\tau) - \Phi_{HF} &\equiv (\hat{I} - \hat{P})(\mathcal{E}_0 - \hat{F})^{-1}(\mathcal{E}_0 - E + \hat{V})\Phi_{HF}(\tau) \\ &\equiv (\hat{I} - \hat{P})(\mathcal{E}_0 - \hat{F})^{-1} \left( \sum_{\mathbf{i}, \mathbf{a}} \Phi_{\mathbf{i}}^{\mathbf{a}}(\tau) \langle \Phi_{\mathbf{i}}^{\mathbf{a}} | (\mathcal{E}_0 - E + \hat{V}) | \Phi_0 \rangle \right) \\ &= (\hat{I} - \hat{P})(\mathcal{E}_0 - \hat{F})^{-1} \left( \sum_{\mathbf{i}, \mathbf{a}} \Phi_{\mathbf{i}}^{\mathbf{a}}(\tau) \left( \langle \Phi_{\mathbf{i}}^{\mathbf{a}} | (\mathcal{E}_0 - E) | \Phi_0 \rangle + \langle \Phi_{\mathbf{i}}^{\mathbf{a}} | \hat{V} | \Phi_0 \rangle \right) \right) \\ &= \sum_{\mathbf{i}, \mathbf{a}} (\hat{I} - \hat{P})(\mathcal{E}_0 - \hat{F})^{-1} \Phi_{\mathbf{i}}^{\mathbf{a}}(\tau) \left[ (\mathcal{E}_0 - E) \langle \Phi_{\mathbf{i}}^{\mathbf{a}} | \Phi_0 \rangle + \langle \Phi_{\mathbf{i}}^{\mathbf{a}} | \hat{V} | \Phi_0 \rangle \right] \\ &= \sum_{\mathbf{i}, \mathbf{a}} (\hat{I} - \hat{P})(\mathcal{E}_0 - \mathcal{E}_{\mathbf{i}}^{\mathbf{a}})^{-1} \Phi_{\mathbf{i}}^{\mathbf{a}}(\tau) \left[ (\mathcal{E}_0 - E) \delta_{\mathbf{ia}} + \langle \Phi_{\mathbf{i}}^{\mathbf{a}} | \hat{V} | \Phi_0 \rangle \right] \\ &= \sum_{\mathbf{i}, \mathbf{a}} \left( (\hat{I} - \hat{P})(\mathcal{E}_0 - E)(\mathcal{E}_0 - \mathcal{E}_{\mathbf{i}}^{\mathbf{a}})^{-1} \Phi_{\mathbf{i}}^{\mathbf{a}}(\tau) \delta_{\mathbf{ia}} \right. \\ &\quad \left. + (\hat{I} - \hat{P})(\mathcal{E}_0 - \mathcal{E}_{\mathbf{i}}^{\mathbf{a}})^{-1} \Phi_{\mathbf{i}}^{\mathbf{a}}(\tau) \langle \Phi_{\mathbf{i}}^{\mathbf{a}} | \hat{V} | \Phi_0 \rangle \right) \\ &= \sum_{\mathbf{i}, \mathbf{a}} \left( (\mathcal{E}_0 - E)(\mathcal{E}_0 - \mathcal{E}_{\mathbf{i}}^{\mathbf{a}})^{-1} \delta_{\mathbf{ia}} (\hat{I} - \hat{P}) \Phi_{\mathbf{i}}^{\mathbf{a}}(\tau) \right. \\ &\quad \left. + \frac{\langle \Phi_{\mathbf{i}}^{\mathbf{a}} | \hat{V} | \Phi_0 \rangle}{\mathcal{E}_0 - \mathcal{E}_{\mathbf{i}}^{\mathbf{a}}} (\hat{I} - \hat{P}) \Phi_{\mathbf{i}}^{\mathbf{a}}(\tau) \right) \end{aligned} \quad (5.93)$$

Here  $\sum_{\mathbf{i}, \mathbf{a}}$  denotes the sum over all unique Slater determinants compare Eq. (5.25), including the

Hartree Fock wave function, which we have chosen to denote  $\Phi_0$  instead of  $\Phi_{\mathbf{i}}^{\mathbf{i}}$  in deference to its special role as the zeroth order approximate wave function in the perturbation series.

Using Eq. (5.75) to evaluate  $(\hat{I} - \hat{P})\Phi_i^a(\tau)$ , we have<sup>30</sup>

$$\begin{aligned}
\Psi^{(1)}(\tau) - \Phi_{HF} &= \sum_{i,a} \left( (\mathcal{E}_0 - E)(\mathcal{E}_0 - \mathcal{E}_i^a)^{-1} \delta_{i,a} (\Phi_i^a(\tau) - \langle \Phi_0 | \Phi_i^a \rangle \Phi_0(\tau)) \right. \\
&\quad \left. + \frac{\langle \Phi_i^a | \hat{V} | \Phi_0 \rangle}{\mathcal{E}_0 - \mathcal{E}_i^a} (\Phi_i^a(\tau) - \langle \Phi_0 | \Phi_i^a \rangle \Phi_0(\tau)) \right) \\
&= \sum_{i,a} (\mathcal{E}_0 - E)(\mathcal{E}_0 - \mathcal{E}_i^a)^{-1} \delta_{i,a} (\Phi_i^a(\tau) - \delta_{ia} \Phi_0(\tau)) \\
&\quad + \sum_{i,a} \frac{\langle \Phi_i^a | \hat{V} | \Phi_0 \rangle}{\mathcal{E}_0 - \mathcal{E}_i^a} (\Phi_i^a(\tau) - \langle \Phi_0 | \Phi_i^a \rangle \Phi_0(\tau)) \\
&= \sum_{i,a} \frac{\mathcal{E}_0 - E}{\mathcal{E}_0 - \mathcal{E}_i^a} \delta_{ia} (\Phi_i^a(\tau) - \delta_{ia} \Phi_0(\tau)) + \sum_{i,a} \frac{\langle \Phi_i^a | \hat{V} | \Phi_0 \rangle}{\mathcal{E}_0 - \mathcal{E}_i^a} (\Phi_i^a(\tau) - \delta_{ia} \Phi_0(\tau)) \\
&= 0 + \underbrace{\frac{\langle \Phi_0 | \hat{V} | \Phi_0 \rangle}{\mathcal{E}_0 - \mathcal{E}_0} (\Phi_0(\tau) - \Phi_0(\tau))}_{\text{HF term; } i=a} + \sum_{i,a} \frac{\langle \Phi_i^a | \hat{V} | \Phi_0 \rangle}{\mathcal{E}_0 - \mathcal{E}_i^a} (\Phi_i^a(\tau) - \delta_{ia} \Phi_0(\tau)) \\
&= 0 + \underbrace{\frac{\langle \Phi_i^a | \hat{V} | \Phi_0 \rangle}{\mathcal{E}_0 - \mathcal{E}_0} (\Phi_0(\tau) - \Phi_0(\tau))}_{\text{HF term; } i=a} + \sum_{i,a} \frac{\langle \Phi_i^a | \hat{V} | \Phi_0 \rangle}{\mathcal{E}_0 - \mathcal{E}_i^a} \Phi_i^a(\tau) \\
&= \sum_{i,a} \frac{\langle \Phi_i^a | \hat{V} | \Phi_0 \rangle}{\mathcal{E}_0 - \mathcal{E}_i^a} \Phi_i^a(\tau)
\end{aligned} \tag{5.94}$$

If we substitute Eq. (5.94) into Eq. (5.87) for  $E_{MBPT}^{(2)}$  and use the result from Eq. (5.88) again (with  $\hat{Q} = \hat{V}$ ), we have that

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<sup>30</sup> The astute reader will note that there are indeterminate  $\frac{0}{0}$  terms in Eq. (5.94). These have been set to zero, which is the correct result in this case. This can be derived either by using a variant of L'Hôpital's rule or, more easily, by performing the previous analysis without first setting  $\mathbb{E}_{MBPT} = \mathcal{E}_0$  (Eq. (5.85)), and performing this last step only once the wave function has been constructed. The fundamental reason for this result is that, by choosing intermediate normalization, we are able to ensure that the first order-correction to the wave function—as well as all the higher-order corrections—were orthogonal to the Hartree-Fock wave function. This is because for *any* function,  $\Xi(\tau)$ , we have that

$$\begin{aligned}
\langle (\hat{I} - \hat{P})\Xi | \Phi_0 \rangle &= \langle \hat{I}\Xi | \Phi_0 \rangle - \langle \hat{P}\Xi | \Phi_0 \rangle \\
&= \langle \Xi | \Phi_0 \rangle - \langle \Xi | \Phi_0 \rangle \langle \Phi_0 | \Phi_0 \rangle \\
&= \langle \Xi | \Phi_0 \rangle - \langle \Xi | \Phi_0 \rangle \langle \Phi_0 | \Phi_0 \rangle \\
&= \langle \Xi | \Phi_0 \rangle - \langle \Xi | \Phi_0 \rangle \\
&= 0
\end{aligned}$$

and, looking at Eq. (5.86), it is clear that every correction to the wave function has this general form.



$$\begin{aligned}
E_{MBPT}^{(2)} &= \mathcal{E}_0 + \left\langle \Phi_0 \left| \hat{V} \left| \left( \Phi_0(\tau) + \sum_{\mathbf{i}, \mathbf{a}} \frac{\langle \Phi_{\mathbf{i}}^{\mathbf{a}} | \hat{V} | \Phi_0 \rangle}{\mathcal{E}_0 - \mathcal{E}_{\mathbf{i}}^{\mathbf{a}}} \Phi_{\mathbf{i}}^{\mathbf{a}}(\tau) \right) \right. \right\rangle \right\rangle. \\
&= \mathcal{E}_0 + \langle \Phi_0 | \hat{V} | \Phi_0 \rangle + \sum_{\mathbf{i}, \mathbf{a}} \frac{\langle \Phi_{\mathbf{i}}^{\mathbf{a}} | \hat{V} | \Phi_0 \rangle}{\mathcal{E}_0 - \mathcal{E}_{\mathbf{i}}^{\mathbf{a}}} \langle \Phi_0 | \hat{V} | \Phi_{\mathbf{i}}^{\mathbf{a}}(\tau) \rangle \\
&= \langle \Phi_0 | \hat{F} | \Phi_0 \rangle + \langle \Phi_0 | \hat{V} | \Phi_0 \rangle + \sum_{\mathbf{i}, \mathbf{a}} \frac{\langle \Phi_0 | \hat{V} | \Phi_{\mathbf{i}}^{\mathbf{a}}(\tau) \rangle \langle \Phi_{\mathbf{i}}^{\mathbf{a}} | \hat{V} | \Phi_0 \rangle}{\mathcal{E}_0 - \mathcal{E}_{\mathbf{i}}^{\mathbf{a}}}
\end{aligned} \tag{5.95}$$

The first term is just the usual zeroth order energy, the second term is just the usual form for the first order energy correction, and the third term is just the usual term for the second order energy correction. We can write Eq. (5.95) in a form that more clearly shows the sense in which the energy is a “correction” to the Hartree-Fock result by writing:

$$\begin{aligned}
E_{MBPT}^{(2)} &= \langle \Phi_0 | \hat{F} + \hat{V} | \Phi_0 \rangle + \sum_{\mathbf{i}, \mathbf{a}} \frac{\langle \Phi_0 | \hat{V} | \Phi_{\mathbf{i}}^{\mathbf{a}} \rangle \langle \Phi_{\mathbf{i}}^{\mathbf{a}} | \hat{V} | \Phi_0 \rangle}{\mathcal{E}_0 - \mathcal{E}_{\mathbf{i}}^{\mathbf{a}}} \\
&= \langle \Phi_0 | \hat{H} | \Phi_0 \rangle + \sum_{\mathbf{i}, \mathbf{a}} \frac{\langle \Phi_0 | \hat{V} | \Phi_{\mathbf{i}}^{\mathbf{a}} \rangle \langle \Phi_{\mathbf{i}}^{\mathbf{a}} | \hat{V} | \Phi_0 \rangle}{\mathcal{E}_0 - \mathcal{E}_{\mathbf{i}}^{\mathbf{a}}} \\
&= E_{HF} + \sum_{\mathbf{i}, \mathbf{a}} \frac{\langle \Phi_0 | \hat{V} | \Phi_{\mathbf{i}}^{\mathbf{a}} \rangle \langle \Phi_{\mathbf{i}}^{\mathbf{a}} | \hat{V} | \Phi_0 \rangle}{\mathcal{E}_0 - \mathcal{E}_{\mathbf{i}}^{\mathbf{a}}}.
\end{aligned} \tag{5.96}$$

Many-Body perturbation theory is a useful technique, and (at second order) it is often fairly accurate. There are two main drawbacks, however.

## A. Many-Body Perturbation Theory is suspect when static correlation is important.

Let us examine the perturbation operator in more detail. We have

$$\begin{aligned}
\hat{V} &\equiv \hat{H} - \hat{F} \\
&= \left( \sum_{i=1}^N \hat{h}(\mathbf{r}_i) + \frac{1}{2} \sum_{i=1}^N \sum_{\substack{j=1 \\ j \neq i}}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right) - \left( \sum_{i=1}^N \hat{f}(\mathbf{r}_i) \right) \\
&= \left( \sum_{i=1}^N \hat{h}(\mathbf{r}_i) + \frac{1}{2} \sum_{i=1}^N \sum_{\substack{j=1 \\ j \neq i}}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right) - \left( \sum_{i=1}^N (\hat{h}(\mathbf{r}_i) + j(\mathbf{r}_i) - \hat{k}(\mathbf{z}_i)) \right) \\
&= \frac{1}{2} \sum_{i=1}^N \sum_{\substack{j=1 \\ j \neq i}}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i=1}^N (j(\mathbf{r}_i) - \hat{k}(\mathbf{z}_i))
\end{aligned} \tag{5.97}$$

Note that  $\hat{V}$  is a difference between a two-electron electron-electron repulsion term from the “true” Hamiltonian,  $\hat{H}$ , and a one-electron term from the Hartree-Fock Hamiltonian,  $\hat{F}$ .

- Recall that for any one-electron operator, then Slater determinants differing by more than a single orbital, and thus Slater determinants differing by more than a single excitation, will be zero.

$$\left\langle \Phi_{ij}^{ab} \left| \sum_{i=1}^N q(\mathbf{r}_i) \right| \Phi_0 \right\rangle = 0 \tag{5.98}$$

- For a two-electron operator, the rule was similar: Slater determinants differing in three or more orbitals, and thus Slater determinants differing by more than a double excitation, will be zero.

$$\left\langle \Phi_{ijk}^{abc} \left| \sum_{i=1}^N \sum_{\substack{j=1 \\ j \neq i}}^N q(\mathbf{r}_i, \mathbf{r}_j) \right| \Phi_0 \right\rangle = 0 \quad (5.99)$$

- We conclude that

$$\left\langle \Phi_{i_1 i_2 i_3 i_4 \dots}^{a_1 a_2 a_3 a_4 \dots} \left| \hat{V} \right| \Phi_0 \right\rangle = 0 \quad i_1 \neq a_1; i_2 \neq a_2; i_3 \neq a_3 \quad (5.100)$$

whenever  $\Phi_i^a$  represents a triple, quadruple, . . . excitation.

Based on this, we see that the first-order wave function, Eq. (5.94), can be written as a sum of singly and doubly excited states,

$$\begin{aligned} \Psi^{(1)}(\tau) &= \Phi_{HF} + \sum_{\mathbf{i}, \mathbf{a}} \frac{\langle \Phi_i^a | \hat{V} | \Phi_0 \rangle}{\epsilon_0 - \epsilon_i^a} \Phi_i^a(\tau) \\ &= \Phi_{HF} + \sum_{i=1}^N \sum_{a=N+1}^{\infty} \frac{\langle \Phi_i^a | \hat{V} | \Phi_0 \rangle}{\epsilon_0 - \epsilon_i^a} \Phi_i^a(\tau) + \sum_{j>i=1}^N \sum_{b>a=N+1}^{\infty} \frac{\langle \Phi_{ij}^{ab} | \hat{V} | \Phi_0 \rangle}{\epsilon_0 - \epsilon_{ij}^{ab}} \Phi_{ij}^{ab}(\tau) \\ &\quad + \sum_{k>j>i=1}^N \sum_{c>b>a=N+1}^{\infty} \frac{\langle \Phi_{ijk}^{abc} | \hat{V} | \Phi_0 \rangle}{\epsilon_0 - \epsilon_{ijk}^{abc}} \Phi_{ijk}^{abc}(\tau) + \dots \end{aligned} \quad (5.101)$$

because all the terms in the second line of Eq. (5.101) are zero. Consequently, we *need* a doubly excited-state determinant to describe the system, as in the Ozone molecule, and thus need triply and quadruply excited state determinants to correlate the excited state, we need to perform an MP4 (= MBPT4) calculation.

First of all, what do we do when, as in a diyl-intermediate of the Cope-rearrangement or the Ozone molecule, there is more than one important Slater determinant. For example, for

## IV. Practical Guidance