I. SLATER DETERMINANTS

Consider a set of N one-electron spin-orbitals $\{\varphi_1, \varphi_2, ...\varphi_{N-1}, \varphi_N\}$. We assume that these functions are orthogonal and normalized, so that $\int \varphi_i^* \varphi_j dV ds = \delta_{ij}$. A properly antisymmetrized product of these N functions can be written as a Slater determinant

$$\Psi(1,2,...,N) = (N!)^{-1/2} \det\{\varphi_1\varphi_2...\varphi_{N-1}\varphi_N\}$$
$$= \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(1) & \varphi_2(1) & \cdots & \varphi_{N-1}(1) & \varphi_N(1) \\ \varphi_1(2) & \varphi_2(2) & \cdots & \varphi_{N-1}(2) & \varphi_N(2) \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ \varphi_1(N-1) & \varphi_2(N-1) & \cdots & \varphi_{N-1}(N-1) & \varphi_N(N-1) \\ \varphi_1(N) & \varphi_2(N) & \cdots & \varphi_{N-1}(N) & \varphi_N(N) \end{vmatrix} \quad (1)$$

Here the rows correspond to the electrons, and the columns, to the spin-orbitals. We will also use the simplified notation

$$\Psi(1,2,...,N) = |\varphi_1\varphi_2...\varphi_{N-1}\varphi_N| \,. \quad (2)$$

We assume that the Hamiltonian can be written as a sum of one-electron (kinetic and potential energy) terms, plus the electron-electron repulsion, summed over all pairs of electrons, namely

$$H(1,2,...,N) = \sum_{i=1}^{N} h(i) + \sum_{i=1}^{N-1}\sum_{j>i} 1/r_{ij} \quad (3)$$

You can show that the expectation value of $H(1,2,...,N)$ is given by

$$\langle \Psi | H | \Psi \rangle = \sum_{i=1}^{N} h_i + \sum_{i=1}^{N-1}\sum_{j=i+1}^{N} \left(\left[\varphi_i^2 \mid \varphi_j^2\right] - \delta_{\sigma_i\sigma_j} \left[\varphi_i\varphi_j \mid \varphi_j\varphi_i\right] \right) \quad (4)$$

where σ is the spin projection quantum number ($\sigma = \pm 1/2$). Here,

$$h_i = \langle \varphi_i | h | \varphi_i \rangle$$

$$\left[\varphi_i^2 \mid \varphi_j^2\right] = \int |\varphi_i(1)|^2 \frac{1}{r_{12}} |\varphi_j(2)|^2 \, dV_1 dV_2$$

and

$$[\varphi_i\varphi_j \mid \varphi_j\varphi_i] = \int \varphi_i^*(1)\varphi_j(1)\frac{1}{r_{12}}\varphi_j^*(2)\varphi_i(2) dV_1 dV_2$$

The first of the two-electron integrals is called a "Coulomb" integral, and is the averaged repulsion between an electron in spin-orbital φ_i and and an electron in spin-orbital φ_j. The second two-electron integral, called an "exchange" integral, is the self-repulsion of the overlap distribution $\varphi_i \times \varphi_j$. This integral has no classical analogue. The Kroenecker δ in Eq. (4) arises because the exchange integral will be non-zero unless the spin-orbitals φ_i and φ_j have the same spin projection quantum number σ.

Thus, the energy of a Slater determinantal wavefunction is a sum of the one-electron energies of all the spin-orbitals, the repulsive Coulomb interaction between all pairs of occupied spin orbitals (between all pairs of electrons) minus an exchange term between all spin-orbitals of the same spin.

Now, let us replace the spin orbitals φ_i and φ_j in the original Slater determinant with two new spin-orbitals χ_i and χ_j to give an new N-electron Slater determinant Φ. We assume that the replacement spin-orbitals are orthonormal and also orthogonal to the replaced orbitals. The coupling matrix element $\langle \Psi | H | \Phi \rangle$ is

$\langle \Psi | H | \Phi \rangle = [\varphi_i \chi_i \,|\, \varphi_j \chi_j]$ if φ_i and χ_i as well as φ_j and χ_j have the same spins;

$\langle \Psi | H | \Phi \rangle = -\,[\varphi_i \chi_j \,|\, \varphi_j \chi_i]$ if φ_i and χ_j as well as φ_j and χ_i have the same spins;

$\langle \Psi | H | \Phi \rangle = 0$, otherwise.

Here

$$[\varphi_i \chi_i \,|\, \varphi_j \chi_j] = \int \varphi_i^*(1) \chi_i(1) \frac{1}{r_{12}} \varphi_j^*(2) \chi_j(2) dV_1 dV_2$$

and

$$[\varphi_i \chi_j \,|\, \varphi_j \chi_i] = \int \varphi_i^*(1) \chi_j(1) \frac{1}{r_{12}} \varphi_j^*(2) \chi_i(2) dV_1 dV_2$$