$$h(i) = -\frac{\hbar^2}{2m}\nabla_i^2 - \sum_A \frac{Z_A}{r_{iA}} \tag{1}$$

$$eer(i,j) = r_{ij}^{-1} \tag{2}$$

$$H^{\text{elect}} = \sum_i h(i) + \sum_{i<j} eer(i,j) \tag{3}$$

Based on the Hartree Product wavefunction

$$\psi_{\text{HP}} = \psi_a(1)\alpha(1)\psi_a(2)\beta(2)\psi_b(3)\alpha(3) \tag{4}$$

we can construct the Slater Determinant as

$$\psi_{\text{SD}} = \frac{1}{\sqrt{6}}[\psi_a(1)\alpha(1)\psi_a(2)\beta(2)\psi_b(3)\alpha(3) + \psi_a(3)\alpha(3)\psi_a(1)\beta(1)\psi_b(2)\alpha(2) \tag{5}$$

$$+\psi_a(2)\alpha(2)\psi_a(3)\beta(3)\psi_b(1)\alpha(1) - \psi_a(2)\alpha(2)\psi_a(1)\beta(1)\psi_b(3)\alpha(3) \tag{6}$$

$$-\psi_a(3)\alpha(3)\psi_a(2)\beta(2)\psi_b(1)\alpha(1) - \psi_a(1)\alpha(1)\psi_a(3)\beta(3)\psi_b(2)\alpha(2)] \tag{7}$$

Now consider

$$\int \psi_{\text{SD}}^* H^{\text{elect}} \psi_{\text{SD}} \tag{8}$$

Here

$$H^{\text{elect}} = h(1) + h(2) + h(3) + eer(1,2) + eer(1,3) + eer(2,3) \tag{9}$$

This will yield 216 terms! Without expanding H^{elect}, there are 36 terms which we can write down

$$(1/6)\int \big(\psi_a^*(1)\alpha^*(1)\psi_a^*(2)\beta^*(2)\psi_b^*(3)\alpha^*(3) + \psi_a^*(3)\alpha^*(3)\psi_a^*(1)\beta^*(1)\psi_b^*(2)\alpha^*(2) \tag{10}$$

$$+\psi_a^*(2)\alpha^*(2)\psi_a^*(3)\beta^*(3)\psi_b^*(1)\alpha^*(1) - \psi_a^*(2)\alpha^*(2)\psi_a^*(1)\beta^*(1)\psi_b^*(3)\alpha^*(3) \tag{11}$$

$$-\psi_a^*(3)\alpha^*(3)\psi_a^*(2)\beta^*(2)\psi_b^*(1)\alpha^*(1) - \psi_a^*(1)\alpha^*(1)\psi_a^*(3)\beta^*(3)\psi_b^*(2)\alpha^*(2)\big)H^{\text{elect}} \tag{12}$$

$$\big(\psi_a(1)\alpha(1)\psi_a(2)\beta(2)\psi_b(3)\alpha(3) + \psi_a(3)\alpha(3)\psi_a(1)\beta(1)\psi_b(2)\alpha(2) \tag{13}$$

$$+\psi_a(2)\alpha(2)\psi_a(3)\beta(3)\psi_b(1)\alpha(1) - \psi_a(2)\alpha(2)\psi_a(1)\beta(1)\psi_b(3)\alpha(3) \tag{14}$$

$$-\psi_a(3)\alpha(3)\psi_a(2)\beta(2)\psi_b(1)\alpha(1) - \psi_a(1)\alpha(1)\psi_a(3)\beta(3)\psi_b(2)\alpha(2)\big) \tag{15}$$

$$
\begin{aligned}
= (1/6)\int &\psi_a^*(1)\alpha^*(1)\psi_a^*(2)\beta^*(2)\psi_b^*(3)\alpha^*(3)H^{\text{elect}}\psi_a(1)\alpha(1)\psi_a(2)\beta(2)\psi_b(3)\alpha(3) && (16)\\
&+\psi_a^*(1)\alpha^*(1)\psi_a^*(2)\beta^*(2)\psi_b^*(3)\alpha^*(3)H^{\text{elect}}\psi_a(3)\alpha(3)\psi_a(1)\beta(1)\psi_b(2)\alpha(2) && (17)\\
&+\psi_a^*(1)\alpha^*(1)\psi_a^*(2)\beta^*(2)\psi_b^*(3)\alpha^*(3)H^{\text{elect}}\psi_a(2)\alpha(2)\psi_a(3)\beta(3)\psi_b(1)\alpha(1) && (18)\\
&-\psi_a^*(1)\alpha^*(1)\psi_a^*(2)\beta^*(2)\psi_b^*(3)\alpha^*(3)H^{\text{elect}}\psi_a(2)\alpha(2)\psi_a(1)\beta(1)\psi_b(3)\alpha(3) && (19)\\
&-\psi_a^*(1)\alpha^*(1)\psi_a^*(2)\beta^*(2)\psi_b^*(3)\alpha^*(3)H^{\text{elect}}\psi_a(3)\alpha(3)\psi_a(2)\beta(2)\psi_b(1)\alpha(1) && (20)\\
&-\psi_a^*(1)\alpha^*(1)\psi_a^*(2)\beta^*(2)\psi_b^*(3)\alpha^*(3)H^{\text{elect}}\psi_a(1)\alpha(1)\psi_a(3)\beta(3)\psi_b(2)\alpha(2) && (21)\\
&+\psi_a^*(3)\alpha^*(3)\psi_a^*(1)\beta^*(1)\psi_b^*(2)\alpha^*(2)H^{\text{elect}}\psi_a(1)\alpha(1)\psi_a(2)\beta(2)\psi_b(3)\alpha(3) && (22)\\
&+\psi_a^*(3)\alpha^*(3)\psi_a^*(1)\beta^*(1)\psi_b^*(2)\alpha^*(2)H^{\text{elect}}\psi_a(3)\alpha(3)\psi_a(1)\beta(1)\psi_b(2)\alpha(2) && (23)\\
&+\psi_a^*(3)\alpha^*(3)\psi_a^*(1)\beta^*(1)\psi_b^*(2)\alpha^*(2)H^{\text{elect}}\psi_a(2)\alpha(2)\psi_a(3)\beta(3)\psi_b(1)\alpha(1) && (24)\\
&-\psi_a^*(3)\alpha^*(3)\psi_a^*(1)\beta^*(1)\psi_b^*(2)\alpha^*(2)H^{\text{elect}}\psi_a(2)\alpha(2)\psi_a(1)\beta(1)\psi_b(3)\alpha(3) && (25)\\
&-\psi_a^*(3)\alpha^*(3)\psi_a^*(1)\beta^*(1)\psi_b^*(2)\alpha^*(2)H^{\text{elect}}\psi_a(3)\alpha(3)\psi_a(2)\beta(2)\psi_b(1)\alpha(1) && (26)\\
&-\psi_a^*(3)\alpha^*(3)\psi_a^*(1)\beta^*(1)\psi_b^*(2)\alpha^*(2)H^{\text{elect}}\psi_a(1)\alpha(1)\psi_a(3)\beta(3)\psi_b(2)\alpha(2) && (27)\\
&+\psi_a^*(2)\alpha^*(2)\psi_a^*(3)\beta^*(3)\psi_b^*(1)\alpha^*(1)H^{\text{elect}}\psi_a(1)\alpha(1)\psi_a(2)\beta(2)\psi_b(3)\alpha(3) && (28)\\
&+\psi_a^*(2)\alpha^*(2)\psi_a^*(3)\beta^*(3)\psi_b^*(1)\alpha^*(1)H^{\text{elect}}\psi_a(3)\alpha(3)\psi_a(1)\beta(1)\psi_b(2)\alpha(2) && (29)\\
&+\psi_a^*(2)\alpha^*(2)\psi_a^*(3)\beta^*(3)\psi_b^*(1)\alpha^*(1)H^{\text{elect}}\psi_a(2)\alpha(2)\psi_a(3)\beta(3)\psi_b(1)\alpha(1) && (30)\\
&-\psi_a^*(2)\alpha^*(2)\psi_a^*(3)\beta^*(3)\psi_b^*(1)\alpha^*(1)H^{\text{elect}}\psi_a(2)\alpha(2)\psi_a(1)\beta(1)\psi_b(3)\alpha(3) && (31)\\
&-\psi_a^*(2)\alpha^*(2)\psi_a^*(3)\beta^*(3)\psi_b^*(1)\alpha^*(1)H^{\text{elect}}\psi_a(3)\alpha(3)\psi_a(2)\beta(2)\psi_b(1)\alpha(1) && (32)\\
&-\psi_a^*(2)\alpha^*(2)\psi_a^*(3)\beta^*(3)\psi_b^*(1)\alpha^*(1)H^{\text{elect}}\psi_a(1)\alpha(1)\psi_a(3)\beta(3)\psi_b(2)\alpha(2) && (33)
\end{aligned}
$$

$$-\psi_a^*(2)\alpha^*(2)\psi_a^*(1)\beta^*(1)\psi_b^*(3)\alpha^*(3)H^{\text{elect}}\psi_a(1)\alpha(1)\psi_a(2)\beta(2)\psi_b(3)\alpha(3) \tag{34}$$

$$-\psi_a^*(2)\alpha^*(2)\psi_a^*(1)\beta^*(1)\psi_b^*(3)\alpha^*(3)H^{\text{elect}}\psi_a(3)\alpha(3)\psi_a(1)\beta(1)\psi_b(2)\alpha(2) \tag{35}$$

$$-\psi_a^*(2)\alpha^*(2)\psi_a^*(1)\beta^*(1)\psi_b^*(3)\alpha^*(3)H^{\text{elect}}\psi_a(2)\alpha(2)\psi_a(3)\beta(3)\psi_b(1)\alpha(1) \tag{36}$$

$$+\psi_a^*(2)\alpha^*(2)\psi_a^*(1)\beta^*(1)\psi_b^*(3)\alpha^*(3)H^{\text{elect}}\psi_a(2)\alpha(2)\psi_a(1)\beta(1)\psi_b(3)\alpha(3) \tag{37}$$

$$+\psi_a^*(2)\alpha^*(2)\psi_a^*(1)\beta^*(1)\psi_b^*(3)\alpha^*(3)H^{\text{elect}}\psi_a(3)\alpha(3)\psi_a(2)\beta(2)\psi_b(1)\alpha(1) \tag{38}$$

$$+\psi_a^*(2)\alpha^*(2)\psi_a^*(1)\beta^*(1)\psi_b^*(3)\alpha^*(3)H^{\text{elect}}\psi_a(1)\alpha(1)\psi_a(3)\beta(3)\psi_b(2)\alpha(2) \tag{39}$$

$$-\psi_a^*(3)\alpha^*(3)\psi_a^*(2)\beta^*(2)\psi_b^*(1)\alpha^*(1)H^{\text{elect}}\psi_a(1)\alpha(1)\psi_a(2)\beta(2)\psi_b(3)\alpha(3) \tag{40}$$

$$-\psi_a^*(3)\alpha^*(3)\psi_a^*(2)\beta^*(2)\psi_b^*(1)\alpha^*(1)H^{\text{elect}}\psi_a(3)\alpha(3)\psi_a(1)\beta(1)\psi_b(2)\alpha(2) \tag{41}$$

$$-\psi_a^*(3)\alpha^*(3)\psi_a^*(2)\beta^*(2)\psi_b^*(1)\alpha^*(1)H^{\text{elect}}\psi_a(2)\alpha(2)\psi_a(3)\beta(3)\psi_b(1)\alpha(1) \tag{42}$$

$$+\psi_a^*(3)\alpha^*(3)\psi_a^*(2)\beta^*(2)\psi_b^*(1)\alpha^*(1)H^{\text{elect}}\psi_a(2)\alpha(2)\psi_a(1)\beta(1)\psi_b(3)\alpha(3) \tag{43}$$

$$+\psi_a^*(3)\alpha^*(3)\psi_a^*(2)\beta^*(2)\psi_b^*(1)\alpha^*(1)H^{\text{elect}}\psi_a(3)\alpha(3)\psi_a(2)\beta(2)\psi_b(1)\alpha(1) \tag{44}$$

$$+\psi_a^*(3)\alpha^*(3)\psi_a^*(2)\beta^*(2)\psi_b^*(1)\alpha^*(1)H^{\text{elect}}\psi_a(1)\alpha(1)\psi_a(3)\beta(3)\psi_b(2)\alpha(2) \tag{45}$$

$$-\psi_a^*(1)\alpha^*(1)\psi_a^*(3)\beta^*(3)\psi_b^*(2)\alpha^*(2)H^{\text{elect}}\psi_a(1)\alpha(1)\psi_a(2)\beta(2)\psi_b(3)\alpha(3) \tag{46}$$

$$-\psi_a^*(1)\alpha^*(1)\psi_a^*(3)\beta^*(3)\psi_b^*(2)\alpha^*(2)H^{\text{elect}}\psi_a(3)\alpha(3)\psi_a(1)\beta(1)\psi_b(2)\alpha(2) \tag{47}$$

$$-\psi_a^*(1)\alpha^*(1)\psi_a^*(3)\beta^*(3)\psi_b^*(2)\alpha^*(2)H^{\text{elect}}\psi_a(2)\alpha(2)\psi_a(3)\beta(3)\psi_b(1)\alpha(1) \tag{48}$$

$$+\psi_a^*(1)\alpha^*(1)\psi_a^*(3)\beta^*(3)\psi_b^*(2)\alpha^*(2)H^{\text{elect}}\psi_a(2)\alpha(2)\psi_a(1)\beta(1)\psi_b(3)\alpha(3) \tag{49}$$

$$+\psi_a^*(1)\alpha^*(1)\psi_a^*(3)\beta^*(3)\psi_b^*(2)\alpha^*(2)H^{\text{elect}}\psi_a(3)\alpha(3)\psi_a(2)\beta(2)\psi_b(1)\alpha(1) \tag{50}$$

$$+\psi_a^*(1)\alpha^*(1)\psi_a^*(3)\beta^*(3)\psi_b^*(2)\alpha^*(2)H^{\text{elect}}\psi_a(1)\alpha(1)\psi_a(3)\beta(3)\psi_b(2)\alpha(2) \tag{51}$$

Most of these terms drop out immediately due to the spin integration. Only 12 of the 36 terms survive, which are

$$= (1/6)\int \psi_a^*(1)\alpha^*(1)\psi_a^*(2)\beta^*(2)\psi_b^*(3)\alpha^*(3)H^{\text{elect}}\psi_a(1)\alpha(1)\psi_a(2)\beta(2)\psi_b(3)\alpha(3) \tag{52}$$

$$-\psi_a^*(1)\alpha^*(1)\psi_a^*(2)\beta^*(2)\psi_b^*(3)\alpha^*(3)H^{\text{elect}}\psi_a(3)\alpha(3)\psi_a(2)\beta(2)\psi_b(1)\alpha(1) \tag{53}$$

$$+\psi_a^*(3)\alpha^*(3)\psi_a^*(1)\beta^*(1)\psi_b^*(2)\alpha^*(2)H^{\text{elect}}\psi_a(3)\alpha(3)\psi_a(1)\beta(1)\psi_b(2)\alpha(2) \tag{54}$$

$$-\psi_a^*(3)\alpha^*(3)\psi_a^*(1)\beta^*(1)\psi_b^*(2)\alpha^*(2)H^{\text{elect}}\psi_a(2)\alpha(2)\psi_a(1)\beta(1)\psi_b(3)\alpha(3) \tag{55}$$

$$+\psi_a^*(2)\alpha^*(2)\psi_a^*(3)\beta^*(3)\psi_b^*(1)\alpha^*(1)H^{\text{elect}}\psi_a(2)\alpha(2)\psi_a(3)\beta(3)\psi_b(1)\alpha(1) \tag{56}$$

$$-\psi_a^*(2)\alpha^*(2)\psi_a^*(3)\beta^*(3)\psi_b^*(1)\alpha^*(1)H^{\text{elect}}\psi_a(1)\alpha(1)\psi_a(3)\beta(3)\psi_b(2)\alpha(2) \tag{57}$$

$$-\psi_a^*(2)\alpha^*(2)\psi_a^*(1)\beta^*(1)\psi_b^*(3)\alpha^*(3)H^{\text{elect}}\psi_a(3)\alpha(3)\psi_a(1)\beta(1)\psi_b(2)\alpha(2) \tag{58}$$

$$+\psi_a^*(2)\alpha^*(2)\psi_a^*(1)\beta^*(1)\psi_b^*(3)\alpha^*(3)H^{\text{elect}}\psi_a(2)\alpha(2)\psi_a(1)\beta(1)\psi_b(3)\alpha(3) \tag{59}$$

$$-\psi_a^*(3)\alpha^*(3)\psi_a^*(2)\beta^*(2)\psi_b^*(1)\alpha^*(1)H^{\text{elect}}\psi_a(1)\alpha(1)\psi_a(2)\beta(2)\psi_b(3)\alpha(3) \tag{60}$$

$$+\psi_a^*(3)\alpha^*(3)\psi_a^*(2)\beta^*(2)\psi_b^*(1)\alpha^*(1)H^{\text{elect}}\psi_a(3)\alpha(3)\psi_a(2)\beta(2)\psi_b(1)\alpha(1) \tag{61}$$

$$-\psi_a^*(1)\alpha^*(1)\psi_a^*(3)\beta^*(3)\psi_b^*(2)\alpha^*(2)H^{\text{elect}}\psi_a(2)\alpha(2)\psi_a(3)\beta(3)\psi_b(1)\alpha(1) \tag{62}$$

$$+\psi_a^*(1)\alpha^*(1)\psi_a^*(3)\beta^*(3)\psi_b^*(2)\alpha^*(2)H^{\text{elect}}\psi_a(1)\alpha(1)\psi_a(3)\beta(3)\psi_b(2)\alpha(2) \tag{63}$$

and in these terms, the spin integrals evaluate to one, giving

$$= (1/6)\int \psi_a^*(1)\psi_a^*(2)\psi_b^*(3)H^{\text{elect}}\psi_a(1)\psi_a(2)\psi_b(3) \tag{64}$$

$$-\psi_a^*(1)\psi_a^*(2)\psi_b^*(3)H^{\text{elect}}\psi_a(3)\psi_a(2)\psi_b(1) \tag{65}$$

$$+\psi_a^*(3)\psi_a^*(1)\psi_b^*(2)H^{\text{elect}}\psi_a(3)\psi_a(1)\psi_b(2) \tag{66}$$

$$-\psi_a^*(3)\psi_a^*(1)\psi_b^*(2)H^{\text{elect}}\psi_a(2)\psi_a(1)\psi_b(3) \tag{67}$$

$$+\psi_a^*(2)\psi_a^*(3)\psi_b^*(1)H^{\text{elect}}\psi_a(2)\psi_a(3)\psi_b(1) \tag{68}$$

$$-\psi_a^*(2)\psi_a^*(3)\psi_b^*(1)H^{\text{elect}}\psi_a(1)\psi_a(3)\psi_b(2) \tag{69}$$

$$-\psi_a^*(2)\psi_a^*(1)\psi_b^*(3)H^{\text{elect}}\psi_a(3)\psi_a(1)\psi_b(2) \tag{70}$$

$$+\psi_a^*(2)\psi_a^*(1)\psi_b^*(3)H^{\text{elect}}\psi_a(2)\psi_a(1)\psi_b(3) \tag{71}$$

$$-\psi_a^*(3)\psi_a^*(2)\psi_b^*(1)H^{\text{elect}}\psi_a(1)\psi_a(2)\psi_b(3) \tag{72}$$

$$+\psi_a^*(3)\psi_a^*(2)\psi_b^*(1)H^{\text{elect}}\psi_a(3)\psi_a(2)\psi_b(1) \tag{73}$$

$$-\psi_a^*(1)\psi_a^*(3)\psi_b^*(2)H^{\text{elect}}\psi_a(2)\psi_a(3)\psi_b(1) \tag{74}$$

$$+\psi_a^*(1)\psi_a^*(3)\psi_b^*(2)H^{\text{elect}}\psi_a(1)\psi_a(3)\psi_b(2) \tag{75}$$

For these terms, think about the different components of H^{elect}

	h(1)	h(2)	h(3)	r_{12}^{-1}	r_{13}^{-1}	r_{23}^{-1}
(64)	✓	✓	✓	✓	✓	✓
(65)	x	x	x	x	✓	x
(66)	✓	✓	✓	✓	✓	✓
(67)	x	x	x	x	x	✓
(68)	✓	✓	✓	✓	✓	✓
(69)	x	x	x	✓	x	x
(70)	x	x	x	x	x	✓
(71)	✓	✓	✓	✓	✓	✓
(72)	x	x	x	x	✓	x
(73)	✓	✓	✓	✓	✓	✓
(74)	x	x	x	✓	x	x
(75)	✓	✓	✓	✓	✓	✓

Consider one of the entries with all ✓, for example (75).

For $h(1)$ in place of H^{elect} in term (75), we get

$$\int \psi_a^*(1) h(1) \psi_a(1) dr_1 \tag{76}$$

which is the kinetic energy of an electron in orbital ψ_a and also its attraction to the nuclei. Actually there are 6 of these terms, which combine with the (1/6) prefactor to give a full contribution.

For r_{12}^{-1} in place of H^{elect} in term (75), we get

$$\int \psi_a^*(1) \psi_b^*(2) r_{12}^{-1} \psi_a(1) \psi_b(2) dr_1 dr_2 \tag{77}$$

which rearranges to

$$\int \psi_a^*(1) \psi_a(1) r_{12}^{-1} \psi_b^*(2) \psi_b(2) dr_1 dr_2 \tag{78}$$

or

$$\int |\psi_a(1)|^2 \, r_{12}^{-1} \, |\psi_b(2)|^2 dr_1 dr_2 \tag{79}$$

which is clearly a J term (Coulomb integral).

Now consider the other kind of entry, for example (74).

For r_{12}^{-1} in place of H^{elect} in term (74), we get

$$\int \psi_a^*(1)\psi_b^*(2)r_{12}^{-1}\psi_a(2)\psi_b(1)dr_1dr_2 \tag{80}$$

which rearranges to

$$\int \psi_a^*(1)\psi_b(1)r_{12}^{-1}\psi_b^*(2)\psi_a(2)dr_1dr_2 \tag{81}$$

which is clearly a K term (exchange integral).

After seeing this, we can understand what is the 1-electron Fock Hamiltonian, which has to include the h operators and also generate the J and K integrals the way we have derived.

This is on page 40 of the Sherrill notes and on page 8+ of the Chem3023 notes.