1 Orthonormality of Slater determinant

$$
\begin{aligned}
|\Psi\rangle &= \frac{1}{\sqrt{N!}} \sum_{i_1\cdots i_N} \epsilon_{i_1\cdots i_N} \phi_{i_1}(\mathbf{r}_i,\sigma_i)\cdots\phi_{i_N}(\mathbf{r}_N,\sigma_N) \\
\implies \langle\Psi|\Psi\rangle &= \frac{1}{N!}\int d\mathbf{r}_1\cdots d\mathbf{r}_N \left[\sum_{i_1\cdots i_N} \epsilon_{i_1\cdots i_N}\phi^*_{i_1}(\mathbf{r}_1,\sigma_1)\cdots\right]\left[\sum_{j_1\cdots j_N}\epsilon_{j_1\cdots j_N}\phi_{j_1}(\mathbf{r}_1,\sigma_1)\cdots\right] \\
&= \frac{1}{N!}\sum_{i_1\cdots i_N}\sum_{j_1\cdots j_N}\epsilon_{i_1\cdots i_N}\epsilon_{j_1\cdots j_N}\left[\int d\mathbf{r}_1\phi^*_{i_1}(\mathbf{r}_1,\sigma_1)\phi_{j_1}(\mathbf{r}_1,\sigma_1)\right]\cdots\left[\int d\mathbf{r}_N\phi^*_{i_N}(\mathbf{r}_N,\sigma_N)\phi_{j_N}(\mathbf{r}_N,\sigma_N)\right]
\end{aligned}
$$

Each integral is a δ_{ij} assuming the orbitals are orthonormal.

$$
\implies \langle\Psi|\Psi\rangle = \frac{1}{N!}\sum_{i_1\cdots i_N}\epsilon^2_{i_1\cdots i_N} = \frac{N!}{N!} = 1
$$

2 Taking overlaps of Slater determinants in a basis

The expression from the § 1 can be generalized to different determinants, and for an arbitrary basis:

$$
\langle\Phi|\Psi'\rangle = \frac{1}{N!}\sum_{i_1\cdots i_N}\sum_{j_1\cdots j_N}\epsilon_{i_1\cdots i_N}\epsilon_{j_1\cdots j_N}\langle\phi_{i_1}|\psi_{j_1}\rangle\cdots\langle\phi_{i_N}|\psi_{j_N}\rangle \tag{1}
$$

The ordering of the first index is irrelevant, and it cancels the prefactor:

$$
\langle\Phi|\Psi'\rangle = \sum_{j_1\cdots j_N}\epsilon_{j_1\cdots j_N}\langle\phi_1|\psi_{j_1}\rangle\cdots\langle\phi_N|\psi_{j_N}\rangle \tag{2}
$$

This is the form of a determinant. In fact, for a determinant expressed in matrix form for a basis, $|\alpha\rangle$ with overlap $S_{\alpha,\alpha'}$, denoted $\Phi_{\alpha i} = \langle\alpha|\phi_i\rangle$,

$$
\langle\Phi|\Psi'\rangle = \text{Det}\ (\Phi^T_{i,\alpha}S_{\alpha,\alpha'}\Psi_{\alpha',j}) \tag{3}
$$

This is because $\Phi^T_{i,\alpha}S_{\alpha,\alpha'}\Psi_{\alpha',j}$ results in a matrix of the overlaps:

$$
\Phi^T_{i,\alpha}S_{\alpha,\alpha'}\Psi_{\alpha',j} = \begin{pmatrix} \langle\phi_1|\psi_1\rangle & \cdots & \langle\phi_1|\psi_N\rangle \\ \vdots & & \vdots \\ \langle\phi_N|\psi_1\rangle & \cdots & \langle\phi_N|\psi_N\rangle \end{pmatrix} \tag{4}
$$

3 Energy of a Slater determinant wavefunction

$$
\begin{aligned}
|\Psi\rangle &= \frac{1}{\sqrt{N!}}\sum_{\{i_\alpha\}}\epsilon_{i_1\cdots i_N}\prod_{\alpha=1}^N\phi_{i_\alpha}(\mathbf{r}_\alpha,\sigma_\alpha) \\
\langle\Phi|\hat{H}|\Phi\rangle &= \langle\Phi|\hat{T}|\Phi\rangle + \langle\Phi|\hat{V}_{\text{ext}}|\Phi\rangle + \langle\Phi|\hat{V}_{\text{int}}|\Phi\rangle + E_{II} \\
\langle\Phi|\hat{T}|\Phi\rangle &= \frac{1}{N!}\sum_{\{i_\alpha\}}\sum_{\{j_\beta\}}\epsilon_{i_1\cdots i_N}\epsilon_{j_1\cdots j_N}\int d\mathbf{r}_1\cdots d\mathbf{r}_N\prod_{\alpha=1}^N\phi^*_{i_\alpha}(\mathbf{r}_\alpha,\sigma_\alpha)\left[\sum_\gamma -\frac{1}{2}\nabla^2_\gamma\right]\prod_{\beta=1}^N\phi_{j_\beta}(\mathbf{r}_\beta,\sigma_\beta)
\end{aligned}
$$

The steps that proceed are: commute all ϕ_{j_β} that commute with each ∇^2_γ, leave the one that doesn't behind. The ones that commute will form an inner product that utilizes orthonormality to ensure $i_\alpha = j_\alpha$. Now we get the same redundancy as when computing the norm, and a simlar simplification follows.

$$\langle\Phi|\hat{T}|\Phi\rangle = -\frac{1}{2}\frac{1}{N!}\sum_{\{i_\alpha\}}\sum_{\{j_\beta\}}\epsilon_{i_1\cdots i_N}\epsilon_{j_1\cdots j_N}\sum_\gamma\int d\mathbf{r}_1\cdots d\mathbf{r}_N\prod_{\alpha\neq\gamma}\phi^*_{i_\alpha}(\mathbf{r}_\alpha,\sigma_\alpha)\prod_{\beta\neq\gamma}\phi_{j_\beta}(\mathbf{r}_\beta,\sigma_\beta)\phi^*_{i_\gamma}(\mathbf{r}_\gamma,\sigma_\gamma)\nabla^2_\gamma\phi_{j_\gamma}(\mathbf{r}_\gamma,\sigma_\gamma)$$

$$= -\frac{1}{2}\frac{1}{N!}\sum_{\{i_\alpha\}}\sum_{\{j_\beta\}}\epsilon_{i_1\cdots i_N}\epsilon_{j_1\cdots j_N}\sum_\gamma\prod_{\alpha\neq\gamma}\left\{\int d\mathbf{r}_\alpha\phi^*_{i_\alpha}(\mathbf{r}_\alpha,\sigma_\alpha)\phi_{j_\alpha}(\mathbf{r}_\alpha,\sigma_\alpha)\right\}\int d\mathbf{r}_\gamma\phi^*_{i_\gamma}(\mathbf{r}_\gamma,\sigma_\gamma)\nabla^2_\gamma\phi_{j_\gamma}(\mathbf{r}_\gamma,\sigma_\gamma)$$

$$= -\frac{1}{2}\frac{1}{N!}\sum_{\{i_\alpha\}}\sum_{\{j_\beta\}}\epsilon_{i_1\cdots i_N}\epsilon_{j_1\cdots j_N}\sum_\gamma\prod_{\alpha\neq\gamma}\delta_{i_\alpha,j_\alpha}\int d\mathbf{r}_\gamma\phi^*_{i_\gamma}(\mathbf{r}_\gamma,\sigma_\gamma)\nabla^2_\gamma\phi_{j_\gamma}(\mathbf{r}_\gamma,\sigma_\gamma)$$

Thus the sum over j_β is consumed, setting all of $i_\alpha = j_\alpha$ for $\alpha\neq\gamma$, however this also determines that $i_\gamma = j_\gamma$ by process of elimination. This produces a sum of $N!$ identical terms.

$$\implies \langle\Phi|\hat{T}|\Phi\rangle = -\frac{1}{2}\sum_\gamma\int d\mathbf{r}_\gamma\phi^*_\gamma(\mathbf{r}_\gamma,\sigma_\gamma)\nabla^2_\gamma\phi_\gamma(\mathbf{r}_\gamma,\sigma_\gamma)$$

Thus the kinetic energy of the product wavefuntion is simply the sum of the kinetic energies of the orbitals. This will occur the same for any one-body property, since for these operators, we can form the inner product that sets the $i_\alpha = j_\alpha$ for all α.

$$\implies \langle\Phi|[\hat{T}+\hat{V}_{\text{ext}}]|\Phi\rangle = \sum_i\int d\mathbf{r}\ \phi^*_i(\mathbf{r},\sigma_i)\left[-\frac{1}{2}\nabla^2 + V_{\text{ext}}(\mathbf{r})\right]\phi_i(\mathbf{r},\sigma_i)$$

For two body operators, something similar happens. Consider $\hat{V}_{\text{int}}$.

$$\langle\Phi|\hat{V}_{\text{int}}|\Phi\rangle = \frac{1}{N!}\sum_{\{i_\alpha\}}\sum_{\{j_\beta\}}\epsilon_{i_1\cdots i_N}\epsilon_{j_1\cdots j_N}\int d\mathbf{r}_1\cdots d\mathbf{r}_N\prod_{\alpha=1}^N\phi^*_{i_\alpha}(\mathbf{r}_\alpha,\sigma_\alpha)\left[\frac{1}{2}\sum_{\gamma\neq\delta}\frac{1}{|\mathbf{r}_\gamma-\mathbf{r}_\delta|}\right]\prod_{\beta=1}^N\phi_{j_\beta}(\mathbf{r}_\beta,\sigma_\beta)$$

$$= \frac{1}{2}\frac{1}{N!}\sum_{\{i_\alpha\}}\sum_{\{j_\beta\}}\epsilon_{i_1\cdots i_N}\epsilon_{j_1\cdots j_N}\sum_{\gamma\neq\delta}\prod_{\alpha\neq\gamma,\delta}\left\{\int d\mathbf{r}_\alpha\phi^*_{i_\alpha}(\mathbf{r}_\alpha,\sigma_\alpha)\phi_{j_\alpha}(\mathbf{r}_\alpha,\sigma_\alpha)\right\}$$

$$\times\int d\mathbf{r}_\gamma d\mathbf{r}_\delta\left[\frac{\phi^*_{i_\gamma}(\mathbf{r}_\gamma,\sigma_\gamma)\phi^*_{i_\delta}(\mathbf{r}_\delta,\sigma_\delta)\phi_{j_\gamma}(\mathbf{r}_\gamma,\sigma_\gamma)\phi_{j_\delta}(\mathbf{r}_\delta,\sigma_\delta)}{|\mathbf{r}_\gamma-\mathbf{r}_\delta|}\right]$$

$$= \frac{1}{2}\frac{1}{N!}\sum_{\{i_\alpha\}}\sum_{\{j_\beta\}}\epsilon_{i_1\cdots i_N}\epsilon_{j_1\cdots j_N}\sum_{\gamma\neq\delta}\prod_{\alpha\neq\gamma,\delta}\delta_{i_\alpha,j_\alpha}\int d\mathbf{r}_\gamma d\mathbf{r}_\delta\left[\frac{\phi^*_{i_\gamma}(\mathbf{r}_\gamma,\sigma_\gamma)\phi^*_{i_\delta}(\mathbf{r}_\delta,\sigma_\delta)\phi_{j_\gamma}(\mathbf{r}_\gamma,\sigma_\gamma)\phi_{j_\delta}(\mathbf{r}_\delta,\sigma_\delta)}{|\mathbf{r}_\gamma-\mathbf{r}_\delta|}\right]$$

Now for $\alpha\neq\gamma,\delta$, $i_\alpha = j_\alpha$, but this time we cannot further deduce that $i_\gamma = j_\gamma$ since there are two options instead: $i_\gamma = j_\gamma$ and $i_\delta = j_\delta$, or $i_\gamma = j_\delta$ and $i_\delta = j_\gamma$. The sum over j_α is consumed by the delta functions (keeping in mind that observation). In the case that $i_\gamma = j_\gamma$, the Levi-Civita symbol becomes squared and the term is positive. In the other case, they differ by an exchange of indices, thus the product is negative.

$$\implies \langle\Phi|\hat{V}_{\text{int}}|\Phi\rangle = \frac{1}{2}\frac{1}{N!}\sum_{\{i_\alpha\}}\sum_{\gamma\neq\delta}\int d\mathbf{r}_\gamma d\mathbf{r}_\delta\left\{\left[\frac{\phi^*_{i_\gamma}(\mathbf{r}_\gamma,\sigma_\gamma)\phi^*_{i_\delta}(\mathbf{r}_\delta,\sigma_\delta)\phi_{i_\gamma}(\mathbf{r}_\gamma,\sigma_\gamma)\phi_{i_\delta}(\mathbf{r}_\delta,\sigma_\delta)}{|\mathbf{r}_\gamma-\mathbf{r}_\delta|}\right]\right.$$

$$\left. - \left[\frac{\phi^*_{i_\gamma}(\mathbf{r}_\gamma,\sigma_\gamma)\phi^*_{i_\delta}(\mathbf{r}_\delta,\sigma_\delta)\phi_{i_\delta}(\mathbf{r}_\gamma,\sigma_\gamma)\phi_{i_\gamma}(\mathbf{r}_\delta,\sigma_\delta)}{|\mathbf{r}_\gamma-\mathbf{r}_\delta|}\right]\right\}$$

$$= \frac{1}{2}\sum_{\gamma\neq\delta}\int d\mathbf{r}_\gamma d\mathbf{r}_\delta\left[\frac{\phi^*_\gamma(\mathbf{r}_\gamma,\sigma_\gamma)\phi^*_\delta(\mathbf{r}_\delta,\sigma_\delta)\phi_\gamma(\mathbf{r}_\gamma,\sigma_\gamma)\phi_\delta(\mathbf{r}_\delta,\sigma_\delta)}{|\mathbf{r}_\gamma-\mathbf{r}_\delta|}\right]$$

$$- \frac{1}{2}\sum_{\gamma\neq\delta}\int d\mathbf{r}_\gamma d\mathbf{r}_\delta\left[\frac{\phi^*_\gamma(\mathbf{r}_\gamma,\sigma_\gamma)\phi^*_\delta(\mathbf{r}_\delta,\sigma_\delta)\phi_\delta(\mathbf{r}_\gamma,\sigma_\gamma)\phi_\gamma(\mathbf{r}_\delta,\sigma_\delta)}{|\mathbf{r}_\gamma-\mathbf{r}_\delta|}\right]$$

$$= \frac{1}{2}\sum_{\gamma,\delta}\int d\mathbf{r}_\gamma d\mathbf{r}_\delta\left[\frac{\phi^*_\gamma(\mathbf{r}_\gamma,\sigma_\gamma)\phi^*_\delta(\mathbf{r}_\delta,\sigma_\delta)\phi_\gamma(\mathbf{r}_\gamma,\sigma_\gamma)\phi_\delta(\mathbf{r}_\delta,\sigma_\delta)}{|\mathbf{r}_\gamma-\mathbf{r}_\delta|}\right]$$

$$- \frac{1}{2}\sum_{\gamma,\delta}\int d\mathbf{r}_\gamma d\mathbf{r}_\delta\left[\frac{\phi^*_\gamma(\mathbf{r}_\gamma,\sigma_\gamma)\phi^*_\delta(\mathbf{r}_\delta,\sigma_\delta)\phi_\delta(\mathbf{r}_\gamma,\sigma_\gamma)\phi_\gamma(\mathbf{r}_\delta,\sigma_\delta)}{|\mathbf{r}_\gamma-\mathbf{r}_\delta|}\right]$$

Putting this analysis together gives us our result.

4 Derivation of the Hartree-Fock equations

I suppress spin degree of freedom for simplicity.

We appoach it via the method of Lagrange multipliers. We vary the $\phi_i^*(\mathbf{r})$ subject to the constraints $\langle\phi_i|\phi_i\rangle = 1$. Basic theory of Lagrange multipliers requires that

$$\delta\langle\Phi|H|\Phi\rangle - \sum_i \delta\langle\phi_i|\phi_i\rangle = 0$$

So varying ϕ_i^*,

$$\begin{aligned}
\delta\langle\Phi|\hat{H}|\Phi\rangle = &\sum_i \int d\mathbf{r}\delta\phi_i^*(\mathbf{r})\left(\hat{T} + \hat{V}_{\text{ext}}(\mathbf{r})\right)\phi_i(\mathbf{r}) \\
&+ \frac{1}{2}\sum_{ij}\int d\mathbf{r}d\mathbf{r}'\frac{\delta\phi_i^*(\mathbf{r})\phi_j^*(\mathbf{r}')\phi_i(\mathbf{r})\phi_j(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \frac{1}{2}\sum_{ij}\int d\mathbf{r}d\mathbf{r}'\frac{\phi_i^*(\mathbf{r})\delta\phi_j^*(\mathbf{r}')\phi_i(\mathbf{r})\phi_j(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \\
&- \frac{1}{2}\sum_{ij}\int d\mathbf{r}d\mathbf{r}'\frac{\delta\phi_i^*(\mathbf{r})\phi_j^*(\mathbf{r}')\phi_j(\mathbf{r})\phi_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} - \frac{1}{2}\sum_{ij}\int d\mathbf{r}d\mathbf{r}'\frac{\phi_i^*(\mathbf{r})\delta\phi_j^*(\mathbf{r}')\phi_j(\mathbf{r})\phi_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}
\end{aligned}$$

The right side two-body terms are identical to the left side up to renaming the summation index and integration variables.

$$\begin{aligned}
\delta\langle\Phi|\hat{H}|\Phi\rangle &= \sum_i \int d\mathbf{r}\delta\phi_i^*(\mathbf{r})\left(\hat{T} + \hat{V}_{\text{ext}}(\mathbf{r})\right)\phi_i(\mathbf{r}) \\
&\quad + \sum_{ij}\int d\mathbf{r}d\mathbf{r}'\frac{\delta\phi_i^*(\mathbf{r})\phi_j^*(\mathbf{r}')\phi_i(\mathbf{r})\phi_j(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} - \sum_{ij}\int d\mathbf{r}d\mathbf{r}'\frac{\delta\phi_i^*(\mathbf{r})\phi_j^*(\mathbf{r}')\phi_j(\mathbf{r})\phi_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \\
&= \sum_i \int d\mathbf{r}\delta\phi_i^*(\mathbf{r})\left\{\left(\hat{T} + \hat{V}_{\text{ext}}\right) + \sum_j\int d\mathbf{r}'\frac{\phi_j^*(\mathbf{r}')\phi_i(\mathbf{r})\phi_j(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} - \sum_j\int d\mathbf{r}'\frac{\phi_j^*(\mathbf{r}')\phi_j(\mathbf{r})\phi_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\right\}
\end{aligned}$$

Thus,

$$\begin{aligned}
&\delta\langle\Phi|H|\Phi\rangle - \sum_i \delta\langle\phi_i|\phi_i\rangle = 0 \\
\iff &\sum_i \int d\mathbf{r}\delta\phi_i^*(\mathbf{r})\left\{\left(\hat{T} + \hat{V}_{\text{ext}}\right)\phi_i(\mathbf{r}) + \sum_j\int d\mathbf{r}'\frac{\phi_j^*(\mathbf{r}')\phi_i(\mathbf{r})\phi_j(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} - \sum_j\int d\mathbf{r}'\frac{\phi_j^*(\mathbf{r}')\phi_j(\mathbf{r})\phi_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} - \varepsilon_i\phi_i(\mathbf{r})\right\} = 0
\end{aligned}$$

Since $\delta\phi_i^*(\mathbf{r})$ is arbitrary, the term in the brackets must be zero for all i. These are the Hartree-Fock equations.

5 Proof of Koopman's theorem

Here are the Hartree-Fock equations written more explicitly:

$$\left[-\frac{1}{2}\nabla^2 + V_{\text{ext}} + \sum_{j,\sigma_j}\int d\mathbf{r}'\frac{\phi_j^{\sigma_j *}(\mathbf{r}')\phi_j^{\sigma_j}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\right]\phi_i^\sigma(\mathbf{r}) - \sum_j\int d\mathbf{r}'\frac{\phi_j^{\sigma_j *}(\mathbf{r}')\phi_i^\sigma(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\phi_j^\sigma(\mathbf{r}) = \varepsilon_i^\sigma\phi_i^\sigma(\mathbf{r}) \tag{5}$$

Taking an inner product of (5) with $\langle\phi_i|$,

$$\begin{aligned}
\varepsilon_i^\sigma &= \int d\mathbf{r}\ \phi_i^*(\mathbf{r})\left\{\left[-\frac{1}{2}\nabla^2 + V_{\text{ext}} + \sum_{j,\sigma_j}\int d\mathbf{r}'\frac{\phi_j^{\sigma_j *}(\mathbf{r}')\phi_j^{\sigma_j}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\right]\phi_i^\sigma(\mathbf{r}) - \sum_j\int d\mathbf{r}'\frac{\phi_j^{\sigma_j *}(\mathbf{r}')\phi_i^\sigma(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\phi_j^\sigma(\mathbf{r})\right\} \\
&= \int d\mathbf{r}\ \phi_i^*(\mathbf{r})\left[\hat{T} + V_{\text{ext}}(\mathbf{r})\right]\phi(\mathbf{r}) + \sum_j\int d\mathbf{r}\ d\mathbf{r}'\frac{\phi_i^*(\mathbf{r})\phi_j^*(\mathbf{r}')\phi_i(\mathbf{r})\phi_j(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} - \sum_j\int d\mathbf{r}\ d\mathbf{r}'\frac{\phi_i^*(\mathbf{r})\phi_j^*(\mathbf{r}')\phi_j(\mathbf{r})\phi_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}
\end{aligned}$$

On the other hand, consider the Slater determinant with the kth orbital missing, denoted $|\Phi^{(k)}_{N-1}\rangle$. (See eq. **??**).

$$
\begin{aligned}
\langle\Phi^{(k)}_{N-1}|\hat{H}|\Phi^{(k)}_{N-1}\rangle = &\sum_{i\neq k}\int d\mathbf{r}\ \phi_i(\mathbf{r})\left[\hat{T}+V_{\text{ext}}(\mathbf{r})\right]\phi_i(\mathbf{r}) \\
&+\frac{1}{2}\sum_{i,j\neq k}\int d\mathbf{r}\ d\mathbf{r}'\ \frac{\phi_i^*(\mathbf{r})\phi_j^*(\mathbf{r}')\phi_i(\mathbf{r})\phi_j(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \\
&-\frac{1}{2}\sum_{i,j\neq k}\int d\mathbf{r}\ d\mathbf{r}'\ \frac{\phi_i^*(\mathbf{r})\phi_j^*(\mathbf{r}')\phi_j(\mathbf{r})\phi_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}
\end{aligned}
$$

The one-body terms come readily, since they are simply missing one term in the sum (when $i = k$). The two-body terms have two series of terms for both the direct and exchange terms that are missing, when $i = k$ and when $j = k$. I'll focus on the direct terms, since the exchange follow for identical reasons.

$$
\begin{aligned}
\implies \langle\Phi^{(k)}_{N-1}|\hat{H}|\Phi^{(k)}_{N-1}\rangle - \langle\Phi|\hat{H}|\Phi\rangle = &-\int d\mathbf{r}\ \phi_k(\mathbf{r})\left[\hat{T}+V_{\text{ext}}(\mathbf{r})\right]\phi_k(\mathbf{r}) \\
&-\frac{1}{2}\sum_j\int d\mathbf{r}\ d\mathbf{r}'\frac{\phi_k^*(\mathbf{r})\phi_j^*(\mathbf{r}')\phi_k(\mathbf{r})\phi_j(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \\
&-\frac{1}{2}\sum_i\int d\mathbf{r}\ d\mathbf{r}'\frac{\phi_i^*(\mathbf{r})\phi_k^*(\mathbf{r}')\phi_i(\mathbf{r})\phi_k(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \\
&+\text{Exchange terms}
\end{aligned}
$$

Now the two direct terms will be identical if we exchange both $\mathbf{r} \leftrightarrow \mathbf{r}'$ in the second integral. The same simplification follows for the exchange term which I neglected to write out.

$$
\begin{aligned}
\implies \langle\Phi^{(k)}_{N-1}|\hat{H}|\Phi^{(k)}_{N-1}\rangle - \langle\Phi|\hat{H}|\Phi\rangle = &-\int d\mathbf{r}\ \phi_k(\mathbf{r})\left[\hat{T}+V_{\text{ext}}(\mathbf{r})\right]\phi_k(\mathbf{r}) \\
&-\sum_j\int d\mathbf{r}\ d\mathbf{r}'\frac{\phi_k^*(\mathbf{r})\phi_j^*(\mathbf{r}')\phi_k(\mathbf{r})\phi_j(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \\
&+\sum_j\int d\mathbf{r}\ d\mathbf{r}'\frac{\phi_k^*(\mathbf{r})\phi_j^*(\mathbf{r}')\phi_j(\mathbf{r})\phi_k(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}
\end{aligned}
$$

which now matches the right hand side of the expression for ε_k. This completes the proof for subtraction of orbitals from the Slater determinant, the same sequence of steps works with adding an orbital, since now $\langle\Phi|\hat{H}|\Phi\rangle$ does not contain the added orbital, and hence the result switches sign.