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Computational Nanoscience: Solution to Exercise Sheet No. 2

Exercise 2.1: Normalization and antisymmetry of Slater determinants

The single particle orbitals are orthonormal, i.e.

$$\int d^3\mathbf{r}\psi_i^*(\mathbf{r})\psi_j(\mathbf{r}) = \delta_{ij}$$

The normalisation of the Slater determinant is evaluated by the resolution of identity in the many-particle basis

$$\begin{aligned}
\langle\Psi_{\text{SD}}|\Psi_{\text{SD}}\rangle &= \frac{1}{N!}\int d^3\mathbf{x}_1 \int d^3\mathbf{x}_2 ... \langle\Psi_{\text{SD}}|\mathbf{x}_1\mathbf{x}_2...\rangle\langle ...\mathbf{x}_2\mathbf{x}_1|\Psi_{\text{SD}}\rangle = \\
&= \frac{1}{N!}\sum_{\sigma,\sigma'} \text{sgn}(\sigma)\text{sgn}(\sigma') \int d^3\mathbf{x}_1 \int d^3\mathbf{x}_2 ... \prod_i \psi^*_{\sigma(i)}(\mathbf{x}_i)\psi_{\sigma'(i)}(\mathbf{x}_i) = \\
&= \frac{1}{N!}\sum_{\sigma,\sigma'} \text{sgn}(\sigma)\text{sgn}(\sigma') \prod_i \delta_{\sigma(i),\sigma'(i)} = \frac{1}{N!}\sum_\sigma (\text{sgn}(\sigma))^2 = 1\,,
\end{aligned}$$

since the number of permutations of N indices is $N!$ and $(\text{sgn}(\sigma))^2 = 1$.
For the second identity, we can directly use the Leibniz formula

$$\Psi_{\text{SD}}(\mathbf{x}_1, ..., \mathbf{x}_i, ..., \mathbf{x}_j, ..., \mathbf{x}_N) = \sum_\sigma \text{sgn}(\sigma)\prod_{k=1}^N \psi_{\sigma(k)}(\mathbf{x}_k)$$

We recognize that swapping positions $\mathbf{x}_i$ and $\mathbf{x}_j$ leads to a different permutation numbering - we effectively do one extra swap, which means that an extra sign is introduced in the determinant formula, as all permutations change parity. Hence

$$\begin{aligned}
\Psi_{\text{SD}}(\mathbf{x}_1, ..., \mathbf{x}_j, ..., \mathbf{x}_i, ..., \mathbf{x}_N) &= \sum_{\sigma'} \text{sgn}(\sigma')\prod_{k=1}^N \psi_{\sigma'(k)}(\mathbf{x}_k) = \\
= \sum_\sigma -\text{sgn}(\sigma)\prod_{k=1}^N \psi_{\sigma(k)}(\mathbf{x}_k) &= -\Psi_{\text{SD}}(\mathbf{x}_1, ..., \mathbf{x}_i, ..., \mathbf{x}_j, ..., \mathbf{x}_N)
\end{aligned}$$

Exercise 2.2: Hartree energy

(a) Integrating the electron density leads to

$$\int d^3\mathbf{r}\; n(\mathbf{r}) = \sum_{i=1}^N \int d^3\mathbf{r}\; |\psi_i(\mathbf{r})|^2 = \sum_{i=1}^N 1 = N\,,$$

since the single particle wavefunctions $\psi_i(\mathbf{r})$ are normalized.

(b) The formula says that in Hartree-Fock, the electron density can be computed as sum of the densities of the spatial part of spin orbitals. That looks reasonable since in quantum mechanics, the total density of non-interacting particles is the sum of the densities of the individual particles.

(c) We have

$$E_{\mathrm{H}} = \frac{e^2}{2}\sum_{n=1}^{N}\sum_{m=1}^{N}(\psi_n\psi_n|\psi_m\psi_m) \overset{\text{lecture notes}}{=} \frac{e^2}{2}\sum_{n=1}^{N}\sum_{m=1}^{N}\iint \frac{\psi_n(\mathbf{r})\,\psi_n(\mathbf{r})\,\psi_m(\mathbf{r}')\,\psi_m(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d^3\mathbf{r}\,d^3\mathbf{r}'$$
$$= \frac{1}{2}\iint \frac{n(\mathbf{r})\,n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d^3\mathbf{r}\,d^3\mathbf{r}',$$

where we used $(\psi_i(\mathbf{r}))^2 = |\psi_i(\mathbf{r})|^2$ because we assumed real-valued $\psi_i(\mathbf{r})$ according to the lecture notes.

(d) The Hartree energy is the classical electrostatic interaction energy of a charge density with itself.

(e) Short answer: The integral is running over $\mathbf{r}$ and $\mathbf{r}'$ and therefore double counts all contributions: The charge density in the volume $d^3\mathbf{r}$ interacts with the charge density in $d^3\mathbf{r}'$ and vice versa. The factor $\frac{1}{2}$ takes care to avoid the double counting. This can be quickly seen for the electron density $n(\mathbf{r}) = \delta(\mathbf{r}-\mathbf{r}_1) + \delta(\mathbf{r}-\mathbf{r}_2)$:

$$E_{\mathrm{H}} = \frac{e^2}{2}\iint \frac{n(\mathbf{r})\,n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d^3\mathbf{r}\,d^3\mathbf{r}' = \frac{e^2}{2}\iint \frac{(\delta(\mathbf{r}-\mathbf{r}_1)+\delta(\mathbf{r}-\mathbf{r}_2))(\delta(\mathbf{r}'-\mathbf{r}_1)+\delta(\mathbf{r}'-\mathbf{r}_2))}{|\mathbf{r}-\mathbf{r}'|}\,d^3\mathbf{r}\,d^3\mathbf{r}'$$
$$= \frac{e^2}{2}\left(\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}+\frac{1}{|\mathbf{r}_2-\mathbf{r}_1|}\right) + \text{combinations } \mathbf{r}_1/\mathbf{r}_1 \text{ and } \mathbf{r}_2/\mathbf{r}_2 \text{ (interaction of electrons with themselves)}$$
$$= \frac{e^2}{|\mathbf{r}_1-\mathbf{r}_2|} + \text{combinations } \mathbf{r}_1/\mathbf{r}_1 \text{ and } \mathbf{r}_2/\mathbf{r}_2 \text{ (interaction of electrons with themselves)}$$

Without the factor $\frac{1}{2}$, the electrostatic interaction between the electron at $\mathbf{r}_1$ and at $\mathbf{r}_2$ would not be the familiar Coulomb interaction of two point charges.

Additional information: If we would have two different charge densities $n_1(\mathbf{r})$ and $n(\mathbf{r}_2)$, then the interaction energy is

$$E = \iint \frac{n_1(\mathbf{r})\,n_2(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d^3\mathbf{r}\,d^3\mathbf{r}'\,.$$

However, if we have $n_1(\mathbf{r}) = n_2(\mathbf{r})$, a factor $\frac{1}{2}$ appears. This factor can be understood, when slowly building up the charge density from zero as $n(\mathbf{r})d\alpha$ with $\int_0^1 n(\mathbf{r})d\alpha = n(\mathbf{r})$. If we have two charge densities, this building up reads

$$E = \int\limits_{\alpha=0}^{1}\iint \frac{(n_1(\mathbf{r})\,d\alpha)\,n_2(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d^3\mathbf{r}\,d^3\mathbf{r}'\,.$$

In case we have the same charge density $n_1(\mathbf{r}) = n_2(\mathbf{r})$, and we add charge density $n_1(\mathbf{r})d\alpha$ to the system, we need to take into account, that there is only a charge density $\alpha n_2(\mathbf{r})$ already present, $0 \le \alpha \le 1$ and not the full $n_2(\mathbf{r})$. So, we have for the interaction energy

$$E = \int\limits_{\alpha=0}^{1}\iint \frac{(n(\mathbf{r})\,d\alpha)\,(\alpha\,n(\mathbf{r}'))}{|\mathbf{r}-\mathbf{r}'|}\,d^3\mathbf{r}\,d^3\mathbf{r}' = \int\limits_{0}^{1}\alpha d\alpha \iint \frac{n(\mathbf{r})\,n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d^3\mathbf{r}\,d^3\mathbf{r}' = \frac{1}{2}\iint \frac{n(\mathbf{r})\,n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d^3\mathbf{r}\,d^3\mathbf{r}'\,.$$

(f) No, consider a hydrogen atom with a single electron. Then, the electrostatic electron-electron interaction is zero but the Hartree energy is non-zero.

(g) No. The short answer is that a large fraction of the correlation energy is electron-electron interaction that is not included in $E_\mathrm{H} + E_\mathrm{x}$. In more detail: As introduced in the lecture, we have

$$E = E_\mathrm{HF} + E_\mathrm{c} \tag{1}$$

where E denotes the groundstate energy, $\hat{H}\Psi = E\Psi$ (Ψ: ground state wavefunction), E_HF the Hartree-Fock energy and $E_\mathrm{c} < 0$ the correlation energy. We can now decompose (neglecting nuclei-nuclei interaction)

$$E = T^\mathrm{exact} + E_\mathrm{Ne}^\mathrm{exact} + E_\mathrm{ee}^\mathrm{exact} \tag{2}$$

with $T^\mathrm{exact} = \langle\Psi|\hat{T}|\Psi\rangle$, $E_\mathrm{Ne}^\mathrm{exact} = \langle\Psi|\hat{V}_\mathrm{Ne}|\Psi\rangle$ and $E_\mathrm{ee}^\mathrm{exact} = \langle\Psi|\hat{V}_\mathrm{ee}|\Psi\rangle$. We can also decompose the Hartree-Fock energy into

$$E_\mathrm{HF} = T^\mathrm{HF} + E_\mathrm{Ne}^\mathrm{HF} + E_\mathrm{ee}^\mathrm{HF} \tag{3}$$

where we have $T^\mathrm{HF} = \langle\Psi_\mathrm{SD}^\mathrm{HF}|\hat{T}|\Psi_\mathrm{SD}^\mathrm{HF}\rangle$, $E_\mathrm{Ne}^\mathrm{HF} = \langle\Psi_\mathrm{SD}^\mathrm{HF}|\hat{V}_\mathrm{Ne}|\Psi_\mathrm{SD}^\mathrm{HF}\rangle$ and $E_\mathrm{ee}^\mathrm{HF} = \langle\Psi_\mathrm{SD}^\mathrm{HF}|\hat{V}_\mathrm{ee}|\Psi_\mathrm{SD}^\mathrm{HF}\rangle = E_\mathrm{H} + E_\mathrm{x}$. With Eq. (1), (2) and (3), we have

$$T^\mathrm{exact} + E_\mathrm{Ne}^\mathrm{exact} + E_\mathrm{ee}^\mathrm{exact} = T^\mathrm{HF} + E_\mathrm{Ne}^\mathrm{HF} + E_\mathrm{H} + E_\mathrm{x} + E_\mathrm{c} \tag{4}$$

$$\Rightarrow E_\mathrm{ee}^\mathrm{exact} = T^\mathrm{HF} - T^\mathrm{exact} + E_\mathrm{Ne}^\mathrm{HF} - E_\mathrm{Ne}^\mathrm{exact} + E_\mathrm{H} + E_\mathrm{x} + E_\mathrm{c}\,. \tag{5}$$

So, in general, we have that the electron-electron interaction is not equal to $E_\mathrm{H} + E_\mathrm{x}$.

For the special case of a hydrogen atom, we have $T^\mathrm{HF} = T^\mathrm{exact}$, $E_\mathrm{Ne}^\mathrm{HF} = E_\mathrm{Ne}^\mathrm{exact}$ and $E_\mathrm{c} = 0$ and hence $E_\mathrm{ee}^\mathrm{exact} = E_\mathrm{H} + E_\mathrm{x}$.

For many molecules and solids, we have $T^\mathrm{HF} \approx T^\mathrm{exact}$ and $E_\mathrm{Ne}^\mathrm{HF} \approx E_\mathrm{Ne}^\mathrm{exact}$ such that

$$E_\mathrm{ee}^\mathrm{exact} \approx E_\mathrm{H} + E_\mathrm{x} + E_\mathrm{c}\,. \tag{6}$$

From upper equation it is apparent that the correlation energy contains electron-electron interaction that is not included in Hartree-Fock.

(h) We insert the definition of the Slater determinant in the definition of the density. Further, we assume real-valued spin orbitals (makes the notation easier) and obtain

$$\begin{aligned}
n(\mathbf{r}) &= N \int d\sigma\, d^3\mathbf{x}_2\, d^3\mathbf{x}_3 \ldots d^3\mathbf{x}_N\, |\Psi(\mathbf{x},\mathbf{x}_2,\mathbf{x}_3,\ldots,\mathbf{x}_N)|^2 \\
&= \int d\sigma\, d^3\mathbf{x}_2\, d^3\mathbf{x}_3 \ldots d^3\mathbf{x}_N\, \frac{1}{(N-1)!}
\begin{vmatrix}
\psi_1(\mathbf{x}) & \psi_2(\mathbf{x}) & \ldots & \psi_N(\mathbf{x}) \\
\psi_1(\mathbf{x}_2) & \psi_2(\mathbf{x}_2) & \ldots & \psi_N(\mathbf{x}_2) \\
\vdots & \vdots & \ddots & \vdots \\
\psi_1(\mathbf{x}_N) & \psi_2(\mathbf{x}_N) & \ldots & \psi_N(\mathbf{x}_N)
\end{vmatrix}
\begin{vmatrix}
\psi_1(\mathbf{x}) & \psi_2(\mathbf{x}) & \ldots & \psi_N(\mathbf{x}) \\
\psi_1(\mathbf{x}_2) & \psi_2(\mathbf{x}_2) & \ldots & \psi_N(\mathbf{x}_2) \\
\vdots & \vdots & \ddots & \vdots \\
\psi_1(\mathbf{x}_N) & \psi_2(\mathbf{x}_N) & \ldots & \psi_N(\mathbf{x}_N)
\end{vmatrix} \\
&= \int d\sigma\, d^3\mathbf{x}_2\, d^3\mathbf{x}_3 \ldots d^3\mathbf{x}_N\, \frac{1}{(N-1)!}\Bigg(\psi_1(\mathbf{x})
\begin{vmatrix}
\psi_2(\mathbf{x}_2) & \ldots & \psi_N(\mathbf{x}_2) \\
\vdots & \ddots & \vdots \\
\psi_2(\mathbf{x}_N) & \ldots & \psi_N(\mathbf{x}_N)
\end{vmatrix}
+ \psi_2(\mathbf{x})
\begin{vmatrix}
\psi_1(\mathbf{x}_2) & \psi_3(\mathbf{x}_2) & \ldots & \psi_N(\mathbf{x}_2) \\
\vdots & \vdots & \ddots & \vdots \\
\psi_1(\mathbf{x}_N) & \psi_3(\mathbf{x}_N) & \ldots & \psi_N(\mathbf{x}_N)
\end{vmatrix} \\
&\qquad + \ldots\Bigg)\Bigg(\psi_1(\mathbf{x})
\begin{vmatrix}
\psi_2(\mathbf{x}_2) & \ldots & \psi_N(\mathbf{x}_2) \\
\vdots & \ddots & \vdots \\
\psi_2(\mathbf{x}_N) & \ldots & \psi_N(\mathbf{x}_N)
\end{vmatrix}
+ \psi_2(\mathbf{x})
\begin{vmatrix}
\psi_1(\mathbf{x}_2) & \psi_3(\mathbf{x}_2) & \ldots & \psi_N(\mathbf{x}_2) \\
\vdots & \vdots & \ddots & \vdots \\
\psi_1(\mathbf{x}_N) & \psi_3(\mathbf{x}_N) & \ldots & \psi_N(\mathbf{x}_N)
\end{vmatrix}
+ \ldots\Bigg)
\end{aligned}$$

We have used for the last line the Laplace expansion of the first row of the determinant. Due to the orthogonality of Slater determinants, we have that the terms from the determinant product $\big(\ldots\big)\big(\ldots\big)$ only give non-vanishing results if the determininants are the same:

$$n(\mathbf{r}) = \int d\sigma\, d^3\mathbf{x}_2\, d^3\mathbf{x}_3 \,\ldots\, d^3\mathbf{x}_N\, \frac{1}{(N-1)!}\Bigg(|\psi_1(\mathbf{x})|^2 \begin{vmatrix} \psi_2(\mathbf{x}_2) & \ldots & \psi_N(\mathbf{x}_2) \\ \vdots & \ddots & \vdots \\ \psi_2(\mathbf{x}_N) & \ldots & \psi_N(\mathbf{x}_N) \end{vmatrix} \begin{vmatrix} \psi_2(\mathbf{x}_2) & \ldots & \psi_N(\mathbf{x}_2) \\ \vdots & \ddots & \vdots \\ \psi_2(\mathbf{x}_N) & \ldots & \psi_N(\mathbf{x}_N) \end{vmatrix}$$

$$+ |\psi_2(\mathbf{x})|^2 \begin{vmatrix} \psi_1(\mathbf{x}_2) & \psi_3(\mathbf{x}_2) & \ldots & \psi_N(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(\mathbf{x}_N) & \psi_3(\mathbf{x}_N) & \ldots & \psi_N(\mathbf{x}_N) \end{vmatrix} \begin{vmatrix} \psi_1(\mathbf{x}_2) & \psi_3(\mathbf{x}_2) & \ldots & \psi_N(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(\mathbf{x}_N) & \psi_3(\mathbf{x}_N) & \ldots & \psi_N(\mathbf{x}_N) \end{vmatrix} + \ldots\Bigg)$$

We carry out the integration over the spin coordinate σ with $\psi_n(\mathbf{x}) = \psi_n(\mathbf{r}) f(\sigma)$ with $\int d\sigma |f(\sigma)|^2 = 1$ and use normalization of the Slater determinant,

$$n(\mathbf{r}) = |\psi_1(\mathbf{r})|^2 \int d^3\mathbf{x}_2\, d^3\mathbf{x}_3 \,\ldots\, d^3\mathbf{x}_N\, \frac{1}{\sqrt{(N-1)!}} \begin{vmatrix} \psi_2(\mathbf{x}_2) & \ldots & \psi_N(\mathbf{x}_2) \\ \vdots & \ddots & \vdots \\ \psi_2(\mathbf{x}_N) & \ldots & \psi_N(\mathbf{x}_N) \end{vmatrix} \frac{1}{\sqrt{(N-1)!}} \begin{vmatrix} \psi_2(\mathbf{x}_2) & \ldots & \psi_N(\mathbf{x}_2) \\ \vdots & \ddots & \vdots \\ \psi_2(\mathbf{x}_N) & \ldots & \psi_N(\mathbf{x}_N) \end{vmatrix}$$

$$+ |\psi_2(\mathbf{r})|^2 \int d^3\mathbf{x}_2\, d^3\mathbf{x}_3 \,\ldots\, d^3\mathbf{x}_N \frac{1}{\sqrt{(N-1)!}} \begin{vmatrix} \psi_1(\mathbf{x}_2) & \psi_3(\mathbf{x}_2) & \ldots & \psi_N(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(\mathbf{x}_N) & \psi_3(\mathbf{x}_N) & \ldots & \psi_N(\mathbf{x}_N) \end{vmatrix}$$

$$\times \frac{1}{\sqrt{(N-1)!}} \begin{vmatrix} \psi_1(\mathbf{x}_2) & \psi_3(\mathbf{x}_2) & \ldots & \psi_N(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(\mathbf{x}_N) & \psi_3(\mathbf{x}_N) & \ldots & \psi_N(\mathbf{x}_N) \end{vmatrix}$$

$$+ \ldots$$

$$= |\psi_1(\mathbf{r})|^2 + |\psi_2(\mathbf{r})|^2 + \ldots = \sum_{n=1}^{N} |\psi_n(\mathbf{r})|^2 \,.$$

Exercise 2.3: Hartree-Fock for bond length and lattice constant

(a) Compute the Hartree-Fock energy for O_2 for various distances of the nuclei. The distance with the lowest Hartree-Fock energy is the Hartree-Fock equilibrium bond distance of O_2.

(b) Similar as O_2: Compute the Hartree-Fock energy for different lattice constants. The lattice constant with the lowest Hartree-Fock energy is the Hartree-Fock equilibrium lattice constant.