Problem Set "Foundations of DFT"

Problem 1 (Slater Determinants for 2 electrons)

Given are four single-electron states $|k, \sigma\rangle$ with $k = 1, 2$ and $\sigma = \uparrow, \downarrow$ which are eigenstates of the single-electron operators for the square of the spin $\hat{\mathbf{s}}^2$ and also eigenfunctions of the $z-$component of the spin $\hat{s}_z$

$$\hat{\mathbf{s}}^2|k,\sigma\rangle = \frac{1}{2}(\frac{1}{2}+1)|k,\sigma\rangle = \frac{3}{4}|k,\sigma\rangle$$
$$\hat{s}_z|k,\uparrow\rangle = \frac{1}{2}|k,\uparrow\rangle \qquad \hat{s}_z|k,\downarrow\rangle = -\frac{1}{2}|k,\downarrow\rangle \tag{1}$$

a) From the given four single-electron states, form all possible 2-electron Slater determinants.

b) The set of Slater determinants of part a) forms a complete basis for the Hilbert space of two electrons in a two-level system. Transform this basis into a basis where all basisfunctions are eigenfunctions of the total spin operators $\hat{\mathbf{S}}^2 = (\hat{\mathbf{s}}_1 + \hat{\mathbf{s}}_2)^2$ and $\hat{S}_z = (\hat{s}_{1,z} + \hat{s}_{2,z})$ where $\hat{\mathbf{s}}_k$ and $\hat{s}_{k,z}$ are the operators for the total spin and for the $z-$component of the spin of electron k, respectively.
<u>Hint:</u> express $\hat{\mathbf{S}}^2$ in terms of the spin ladder operators $\hat{s}_k^+ = \hat{s}_{k,x} + i\hat{s}_{k,y}$ and $\hat{s}_k^- = \hat{s}_{k,x} - i\hat{s}_{k,y}$ for electron k.

Problem 2 (Wavefunctions for non-interacting electrons)

The Hamiltonian for N non-interacting electrons in a potential $v(\mathbf{r})$ is

$$\hat{H}_0 = \sum_{j=1}^{N}\left(-\frac{\nabla_j^2}{2} + v(\mathbf{r}_j)\right) \ . \tag{2}$$

Given are the orthonormal eigenfunctions $\varphi_n(\mathbf{r},\sigma)$ of the single-particle problem

$$\hat{h}\varphi_n = \left(-\frac{\nabla^2}{2} + v(\mathbf{r})\right)\varphi_n(\mathbf{r},\sigma) = \varepsilon_n\varphi_n(\mathbf{r},\sigma) \tag{3}$$

with

$$\sum_\sigma \int d^3r \varphi_{n_1}^*(\mathbf{r},\sigma)\varphi_{n_2}(\mathbf{r},\sigma) = \delta_{n_1,n_2} \ . \tag{4}$$

a) Show that the product wavefunction

$$\begin{aligned}\Phi(\mathbf{r}_1,\sigma_1,\ldots,\mathbf{r}_N,\sigma_N) &= \varphi_{n_1}(\mathbf{r}_1,\sigma_1)\varphi_{n_2}(\mathbf{r}_2,\sigma_2)\ldots\varphi_{n_N}(\mathbf{r}_N,\sigma_N)\\ &= \varphi_{n_1}(1)\varphi_{n_2}(2)\ldots\varphi_{n_N}(N)\end{aligned} \tag{5}$$

is a normalized eigenfunction of $\hat{H}_0$ with eigenvalue $E = \varepsilon_{n_1} + \varepsilon_{n_2} + \ldots + \varepsilon_{n_N}$.

Please turn!

b) Use the result of a) to show that the Slater determinant

$$\Phi^{SD}(\mathbf{r}_1, \sigma_1, \ldots, \mathbf{r}_N, \sigma_N) = \frac{1}{\sqrt{N!}} \sum_P (-1)^P \varphi_{n_1}(P_1)\varphi_{n_2}(P_2)\ldots\varphi_{n_N}(P_N) \qquad (6)$$

also is a normalized eigenfunction of $\hat{H}_0$ with the same eigenvalue E. Also show that the density of Φ^{SD} is

$$n(\mathbf{r}) = \sum_\sigma \sum_{j=1}^{N} |\varphi_{n_j}(\mathbf{r}, \sigma)|^2 \,. \qquad (7)$$