Quantum Mechanics II

Exercise 6: Second quantization. N-body problems – Solutions

8 November 2017

1. Express two-particle operator $\hat{F} = \frac{1}{2}\sum_{\alpha\neq\beta} \hat{f}^{(2)}(x_\alpha; x_\beta)$ in terms of creation and annihilation operators for the case of bosons as well as fermions.

   Reminder: $\sum_{\alpha=1}^{N} |i\rangle_\alpha \langle j|_\alpha = a_i^\dagger a_j$.

   Solution: Many-particle systems are described by states in the tensor product of one-particle Hilbert spaces. Let $\{|i\rangle\}$ be an orthonormal basis in the one-particle Hilbert space. The matrix form of two-particle operator $\hat{f}^{(2)}$ in the tensor product space of two particles is:

$$\hat{f}^{(2)} = \sum_{ijkl} |i,j\rangle\langle i,j|\hat{f}^{(2)}|k,l\rangle\langle k,l| = \sum_{ijkl} f_{ijkl}|i,j\rangle\langle k,l|$$

   Bosons (fermions) are identical particles therefore for any pair of bosons (fermions) operator $\hat{f}^{(2)}$ will have the same form. Then for the full operator we have

$$\begin{aligned}
\hat{F} &= \frac{1}{2}\sum_{\alpha\neq\beta}\left(\sum_{ijkl} f_{ijkl}|i,j\rangle_{\alpha,\beta}\langle k,l|_{\alpha,\beta}\right) = \frac{1}{2}\sum_{ijkl} f_{ijkl}\sum_{\alpha\neq\beta}|i\rangle_\alpha\langle k_\alpha| \otimes |j\rangle_\beta\langle l|_\beta \\
&= \frac{1}{2}\sum_{ijkl} f_{ijkl}\left(\left(\sum_\alpha |i\rangle_\alpha\langle k_\alpha|\right)\otimes\left(\sum_\beta |j\rangle_\beta\langle l|_\beta\right) - \sum_\beta |i\rangle_\beta \underbrace{\langle k|j\rangle_\beta}_{\delta_{jk}}\langle l|_\beta\right) \\
&= \frac{1}{2}\sum_{ijkl} f_{ijkl}\left(\hat{a}_i^\dagger\hat{a}_k\hat{a}_j^\dagger\hat{a}_l - \hat{a}_i^\dagger\delta_{jk}\hat{a}_l\right),
\end{aligned}$$

   where in the second line we have taken into account the terms corresponding to the interaction of particle with itself as shown in Fig. 1. In the last term, we can replace $\delta_{jk} = [\hat{a}_k, \hat{a}_j^\dagger]$ (for bosons) and $\delta_{jk} = \{\hat{a}_k, \hat{a}_j^\dagger\}$ (for fermions). Thus we obtain:

$$\begin{aligned}
\hat{F} &= \frac{1}{2}\sum_{ijkl} f_{ijkl}\,\hat{a}_i^\dagger\left(\hat{a}_k a_j^\dagger - \hat{a}_k\hat{a}_j^\dagger \pm \hat{a}_j^\dagger\hat{a}_k\right)\hat{a}_l \\
&= \pm\frac{1}{2}\sum_{ijkl} f_{ijkl}\,\hat{a}_i^\dagger\hat{a}_j^\dagger\underbrace{\hat{a}_k\hat{a}_l}_{\pm\hat{a}_l\hat{a}_k} = \frac{1}{2}\sum_{ijkl} f_{ijkl}\,\hat{a}_i^\dagger a_j^\dagger\hat{a}_l\hat{a}_k \,\blacksquare
\end{aligned}$$

   Note that the order of the sums of operators (first the sum over β and then the sum over α) was chosen arbitrary. It is easy to see that the opposite choice would lead to the exchange of indices of creation and annihilation operators in the final expression as follows $i \leftrightarrow j$ and $k \leftrightarrow l$. However, by commuting two pairs of operators $\hat{a}_j^\dagger\hat{a}_i^\dagger = \pm\hat{a}_i^\dagger\hat{a}_j^\dagger$ and $\hat{a}_k\hat{a}_l = \pm\hat{a}_l\hat{a}_k$ the original result can be we recovered without any change of sign for both, bosons and fermions.

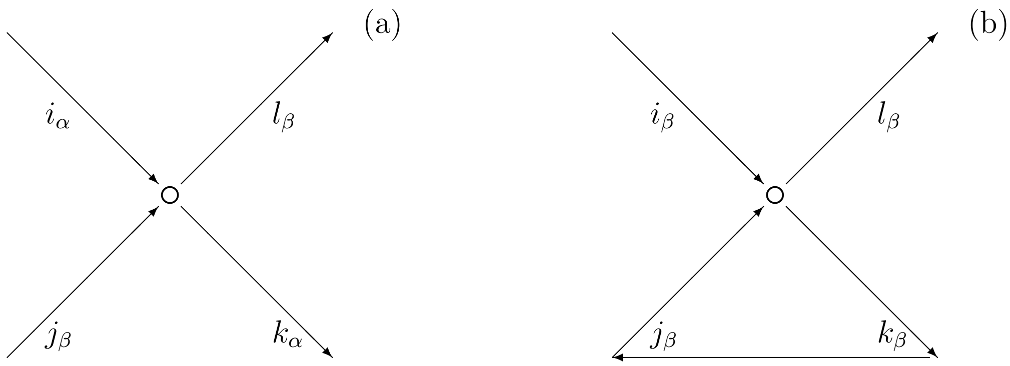

Figure 1: Interaction of two particles (a) and selfinteraction (b).

2. Show that the number operator $\hat{N} = \sum_i \hat{a}_i^\dagger \hat{a}_i$ (for bosons and fermions) commute with the Hamiltonian

$$\hat{H} = \sum_{jk} \hat{a}_j^\dagger \langle i|T|k\rangle \hat{a}_k + \frac{1}{2} \sum_{jklm} \hat{a}_j^\dagger \hat{a}_k^\dagger \langle jk|V|lm\rangle \hat{a}_m \hat{a}_l .$$

<u>Solution:</u> We will check the commutation with each term of the Hamiltonian.

$$\begin{aligned}
\left[\hat{N}, \sum_{jk} \hat{a}_j^\dagger T_{jk} \hat{a}_k\right] &= \sum_{ijk} T_{jk} [\hat{a}_i^\dagger \hat{a}_i, \hat{a}_j^\dagger \hat{a}_k] = \sum_{ijk} T_{jk} (\hat{a}_i^\dagger \underbrace{\hat{a}_i \hat{a}_j^\dagger}_{\delta_{ij} \pm \hat{a}_j^\dagger \hat{a}_i} \hat{a}_k - \hat{a}_j^\dagger \underbrace{\hat{a}_k \hat{a}_i^\dagger}_{\delta_{ik} \pm \hat{a}_i^\dagger \hat{a}_k} \hat{a}_i) \\
&= \sum_{ijk} T_{jk} (\delta_{ij} \hat{a}_i^\dagger \hat{a}_k - \delta_{ik} \hat{a}_j^\dagger \hat{a}_i) \pm \sum_{ijk} T_{jk} (\hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_i \hat{a}_k - \hat{a}_j^\dagger \hat{a}_i^\dagger \hat{a}_k \hat{a}_i) \\
&= \sum_{jk} T_{jk} (\underbrace{\hat{a}_j^\dagger \hat{a}_k - \hat{a}_j^\dagger \hat{a}_k}_{0}) \pm \sum_{ijk} T_{jk} (\hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_i \hat{a}_k - (\pm \hat{a}_i^\dagger \hat{a}_j^\dagger)(\pm \hat{a}_i \hat{a}_k)) \\
&= \pm \sum_{ijk} T_{jk} (\underbrace{\hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_i \hat{a}_k - \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_i \hat{a}_k}_{0}) = 0 \,.
\end{aligned}$$

$$\begin{aligned}
\left[\hat{N}, \sum_{jklm} \hat{a}_j^\dagger \hat{a}_k^\dagger \langle jk|V|lm\rangle \hat{a}_m \hat{a}_l\right] &= \sum_{ijkm} V_{jklm} [\hat{a}_i^\dagger \hat{a}_i, \hat{a}_j^\dagger \hat{a}_k^\dagger \hat{a}_m \hat{a}_l] \\
&= \sum_{ijklm} V_{jklm} (\hat{a}_i^\dagger \underbrace{\hat{a}_i \hat{a}_j^\dagger}_{\delta_{ij} \pm \hat{a}_j^\dagger \hat{a}_i} \hat{a}_k^\dagger \hat{a}_m \hat{a}_l - \hat{a}_j^\dagger \hat{a}_k^\dagger \hat{a}_m \underbrace{\hat{a}_l \hat{a}_i^\dagger}_{\delta_{il} \pm \hat{a}_i^\dagger \hat{a}_l} \hat{a}_i) \\
&= \sum_{ijklm} V_{jklm} (\delta_{ij} \hat{a}_i^\dagger \hat{a}_k^\dagger \hat{a}_m \hat{a}_l - \delta_{il} \hat{a}_j^\dagger \hat{a}_k^\dagger \hat{a}_m \hat{a}_i) \\
&\pm \sum_{ijklm} V_{jklm} (\hat{a}_i^\dagger \hat{a}_j^\dagger \underbrace{\hat{a}_i \hat{a}_k^\dagger}_{\delta_{ik} \pm a_k^\dagger \hat{a}_i} \hat{a}_m \hat{a}_l - \hat{a}_j^\dagger \hat{a}_k^\dagger \underbrace{\hat{a}_m \hat{a}_i^\dagger}_{\delta_{im} \pm a_i^\dagger \hat{a}_m} \hat{a}_l \hat{a}_i) \\
&= \sum_{jklm} V_{jklm} (\underbrace{a_j^\dagger \hat{a}_k^\dagger \hat{a}_m \hat{a}_l - \hat{a}_j^\dagger \hat{a}_k^\dagger \hat{a}_m \hat{a}_l}_{0})
\end{aligned}$$

$$
\begin{aligned}
&\pm \sum_{ijklm} V_{jklm}(\delta_{ik}\hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_m \hat{a}_l - \delta_{im}\hat{a}_j^\dagger \hat{a}_k^\dagger \hat{a}_l \hat{a}_i) \\
&+ \sum_{ijklm} V_{jklm}(\hat{a}_i^\dagger \hat{a}_j^\dagger a_k^\dagger \hat{a}_i \hat{a}_m \hat{a}_l - \hat{a}_j^\dagger \underbrace{\hat{a}_k^\dagger \hat{a}_i^\dagger}_{\pm \hat{a}_i^\dagger \hat{a}_k^\dagger} \hat{a}_m \underbrace{\hat{a}_l \hat{a}_i}_{\pm \hat{a}_i \hat{a}_l}) \\
= &\pm \sum_{jklm} V_{jklm}(\hat{a}_k^\dagger \hat{a}_j^\dagger \hat{a}_m \hat{a}_l - \underbrace{\hat{a}_j^\dagger \hat{a}_k^\dagger}_{\pm a_k^\dagger \hat{a}_j^\dagger} \underbrace{\hat{a}_l \hat{a}_m}_{\pm \hat{a}_m \hat{a}_l}) \\
&+ \sum_{ijklm} V_{jklm}(\hat{a}_i^\dagger \hat{a}_j^\dagger a_k^\dagger \hat{a}_i \hat{a}_m \hat{a}_l - \underbrace{\hat{a}_j^\dagger \hat{a}_i^\dagger}_{\pm \hat{a}_i^\dagger \hat{a}_j^\dagger} \hat{a}_k^\dagger \underbrace{\hat{a}_m \hat{a}_i}_{\pm \hat{a}_i \hat{a}_m} \hat{a}_l) \\
= &\pm \sum_{jklm} V_{jklm}\underbrace{(\hat{a}_k^\dagger \hat{a}_j^\dagger \hat{a}_m \hat{a}_l - a_k^\dagger \hat{a}_j^\dagger \hat{a}_m \hat{a}_l)}_{0} \\
&+ \sum_{ijklm} V_{jklm}\underbrace{(\hat{a}_i^\dagger \hat{a}_j^\dagger a_k^\dagger \hat{a}_i \hat{a}_m \hat{a}_l - \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_k^\dagger \hat{a}_i \hat{a}_m \hat{a}_l)}_{0} = 0 \blacksquare
\end{aligned}
$$

3. Is the sum of ionization energies found by Hartree approximation equal to the total energy (binding energy of atom)?

   Solution: The Lagrange multipliers appear in the variational solution of the Hartree approximation as individual energies:

$$\varepsilon_i = \int \mathrm{d}\mathbf{r}\, \phi_i^*(\mathbf{r}) \left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{r} + V_i(\mathbf{r}) \right) \phi_i(\mathbf{r}),$$

   where

$$V_i(\mathbf{r}) = \sum_{j \neq i} \int \mathrm{d}\mathbf{r}' \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} |\phi_j(\mathbf{r}')|^2.$$

   If we take the electrons from the atom one by one and each time count the ionization energy as ε_i this would correspond to an assumption that the ionization energy of electron is not changed after one electron is removed from the atom.

   In reality, the binding energy of atom is

$$
\begin{aligned}
E_0 &= \langle \hat{H} \rangle = \sum_i \int \mathrm{d}\mathbf{r} \phi_i^*(\mathbf{r}) \left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{r} \right) \phi_i(\mathbf{r}) \\
&+ \frac{1}{2} \sum_i \int \mathrm{d}\mathbf{r}\, \phi_i^*(\mathbf{r}) V_i(\mathbf{r}) \phi_i(\mathbf{r}) \\
&= \sum_i \int \mathrm{d}\mathbf{r}\, \phi_i^*(\mathbf{r}) \left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{r} + V_i(\mathbf{r}) \right) \phi_i(\mathbf{r}) \\
&- \frac{1}{2} \sum_i \int \mathrm{d}\mathbf{r}\, |\phi_i(\mathbf{r})|^2 V_i(\mathbf{r}) \\
&= \sum_i \left[\varepsilon_i - \underbrace{\sum_{i<j} \int \mathrm{d}\mathbf{r} \int \mathrm{d}\mathbf{r}'\, |\phi_i(\mathbf{r})|^2 |\phi_i(\mathbf{r}')|^2 \frac{e^2}{|\mathbf{r} - \mathbf{r}'|}}_{\text{correction term}} \right].
\end{aligned}
$$

Factor 1/2 in the second line is necessary because in the original expression for $\hat{H}$ the sum is $\sum_{i<j}$ whereas V_i is defined with the sum $\sum_{j\neq i}$.

4. Beryllium atom ($Z = 4$)

a) Find the fundamental state of the neutral atom. Write down the state using Slater determinant.

<u>Solution:</u> The fundamental level of Be is

$$Be \,:\, 1s^2 2s^2$$

It can be represented in terms of Sater's determinant as

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \mathbf{x}_4) = \frac{1}{\sqrt{4!}} \begin{vmatrix} \psi_1(\mathbf{x}_1) & \psi_1(\mathbf{x}_2) & \psi_1(\mathbf{x}_3) & \psi_1(\mathbf{x}_4) \\ \psi_2(\mathbf{x}_1) & \psi_2(\mathbf{x}_2) & \psi_2(\mathbf{x}_3) & \psi_2(\mathbf{x}_4) \\ \psi_3(\mathbf{x}_1) & \psi_3(\mathbf{x}_2) & \psi_3(\mathbf{x}_3) & \psi_3(\mathbf{x}_4) \\ \psi_4(\mathbf{x}_1) & \psi_4(\mathbf{x}_2) & \psi_4(\mathbf{x}_3) & \psi_4(\mathbf{x}_4) \end{vmatrix},$$

where

$$\begin{cases} \psi_1(\mathbf{x}_1) = \phi_1(\mathbf{r})|\uparrow\rangle = r^{-1}u_{1s}(r)Y_0^0(\Omega)|\uparrow\rangle \\ \psi_2(\mathbf{x}_1) = \phi_2(\mathbf{r})|\downarrow\rangle = r^{-1}u_{1s}(r)Y_0^0(\Omega)|\downarrow\rangle \\ \psi_3(\mathbf{x}_1) = \phi_3(\mathbf{r})|\uparrow\rangle = r^{-1}u_{2s}(r)Y_0^0(\Omega)|\uparrow\rangle \\ \psi_4(\mathbf{x}_1) = \phi_4(\mathbf{r})|\downarrow\rangle = r^{-1}u_{2s}(r)Y_0^0(\Omega)|\downarrow\rangle, \end{cases}$$

and

$$\begin{cases} |\uparrow\rangle = \chi_{+1/2} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \\ |\downarrow\rangle = \chi_{-1/2} = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \end{cases}$$

are spinors.

b) Write down Hartree-Fock equations taking into account only kinetic energy of electrons and Coulomb's interaction. How many independent equations exist for the fundamental state? Explicit the exchange and coulomb's terms.

<u>Solution:</u> The Hartree-Fock equation is

$$\left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{r}\right)\phi_i(\mathbf{r}) + V_i(\mathbf{r}) = \varepsilon_i\phi_i(\mathbf{r})$$

where the interaction potential is expressed as follows

$$V_i(\mathbf{r}) = \int \mathrm{d}\mathbf{r}' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} \sum_{j=1}^{4} |\phi_j^*(\mathbf{r}')|^2 \phi_i(\mathbf{r}) - \delta_{m_{si},m_{sj}} \int \mathrm{d}\mathbf{r}' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} \sum_{j=1}^{4} \phi_j^*(\mathbf{r}')\phi_i(\mathbf{r}')\phi_j(\mathbf{r})$$

where m_{si} and m_{sj} represent spin projections. The first term is the classical coulomb repulsion potential representing mean-field. The second term representing exchange interaction is non zero only for $m_{si} = m_{sj}$. Then we can rewrite the Hartree-Fock equation as:

$$\begin{aligned} \left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{r}\right)\phi_i(\mathbf{r}) \quad &+ \quad \int \mathrm{d}\mathbf{r}' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} \sum_{j=1}^{4} |\phi_j^*(\mathbf{r}')|^2 \phi_i(\mathbf{r}) \\ &- \quad \delta_{m_{si},m_{sj}} \int \mathrm{d}\mathbf{r}' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} \sum_{j=1}^{4} \phi_j^*(\mathbf{r}')\phi_i(\mathbf{r}')\phi_j(\mathbf{r}) = \varepsilon_i\phi_i(\mathbf{r}), \end{aligned}$$

where we have simplified the spinor components because spin does not modify the equations. Observing the wave functions entering Slater's determinant we have:

$$\begin{cases} \phi_1(\mathbf{r}) & = & \phi_2(\mathbf{r}) \\ \phi_3(\mathbf{r}) & = & \phi_4(\mathbf{r}), \end{cases}$$

and

$$\begin{cases} m_{s1} & = & m_{s3} \\ m_{s2} & = & m_{s4}, \end{cases}$$

We have then for ε_1:

$$\begin{aligned} &\left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{r}\right)\phi_1(\mathbf{r}) \\ &+ \int d\mathbf{r}' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\left(\cancel{|\phi_1(\mathbf{r}')|^2} + \underbrace{|\phi_2(\mathbf{r}')|^2}_{|\phi_1(\mathbf{r}')|^2} + |\phi_3(\mathbf{r}')|^2 + \underbrace{|\phi_4(\mathbf{r}')|^2}_{|\phi_3(\mathbf{r}')|^2}\right)\phi_1(\mathbf{r}) \\ &- \int d\mathbf{r}' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\left(\cancel{\phi_1^*(\mathbf{r}')\phi_1(\mathbf{r}')\phi_1(\mathbf{r})} + \phi_3^*(\mathbf{r}')\phi_1(\mathbf{r}')\phi_3(\mathbf{r})\right) = \varepsilon_1\phi_1(\mathbf{r}), \end{aligned}$$

or after simplification

$$\begin{aligned} &\left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{r}\right)\phi_1(\mathbf{r}) \\ &+ \int d\mathbf{r}' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\left(|\phi_1(\mathbf{r}')|^2 + 2|\phi_3(\mathbf{r}')|^2\right)\phi_1(\mathbf{r}) \\ &- \int d\mathbf{r}' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\phi_3^*(\mathbf{r}')\phi_1(\mathbf{r}')\phi_3(\mathbf{r}) = \varepsilon_1\phi_1(\mathbf{r}), \end{aligned}$$

Now denoting Coulomb's term $V_{C1}(\mathbf{r})$ and the exchange term $V_{ex1}(\mathbf{r})$

$$\begin{aligned} V_{C1}(\mathbf{r}) &= \int d\mathbf{r}' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\left(|\phi_1(\mathbf{r}')|^2 + 2|\phi_3(\mathbf{r}')|^2\right), \\ V_{ex1}(\mathbf{r}) &= -\int d\mathbf{r}' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\phi_3^*(\mathbf{r}')\phi_1(\mathbf{r}'), \end{aligned}$$

we come to the equation

$$\left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{r} + V_{C1}(\mathbf{r})\right)\phi_1(\mathbf{r}) + V_{ex1}(\mathbf{r})\phi_3(\mathbf{r}) = \varepsilon_1\phi_1(\mathbf{r}).$$

The solution for ε_3 is found in the same way, which leads to equation:

$$\left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{r} + V_{C3}(\mathbf{r})\right)\phi_3(\mathbf{r}) + V_{ex3}(\mathbf{r})\phi_1(\mathbf{r}) = \varepsilon_3\phi_3(\mathbf{r}),$$

where $V_{C3}(\mathbf{r})$ is Coulomb's term and $V_{ex3}(\mathbf{r})$ is the exchange term

$$\begin{aligned} V_{C3}(\mathbf{r}) &= \int d\mathbf{r}' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\left(2|\phi_1(\mathbf{r}')|^2 + |\phi_3(\mathbf{r}')|^2\right), \\ V_{ex3}(\mathbf{r}) &= -\int d\mathbf{r}' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\phi_1^*(\mathbf{r}')\phi_3(\mathbf{r}') = V_{ex1}^*(\mathbf{r}). \end{aligned}$$

c) Show that Hartree-Fock equations depend only on the radial coordinate.

<u>Reminder:</u>

$$\frac{1}{|\mathbf{r}-\mathbf{r}'|} = \sum_{l=0}^{\infty} \frac{r_m^l}{r_M^l} P_l(\cos\theta),$$

where $r_m = \min(|\mathbf{r}|, |\mathbf{r}'|)$, $r_M = \max(|\mathbf{r}|, |\mathbf{r}'|)$, and θ is the angle between $\mathbf{r}$ and $\mathbf{r}'$. Functions $P_l(x)$ obey

$$\int_{-1}^{1} P_l(x)dx = 2\delta_{0l}.$$

<u>Solution:</u> The three dimensional integral in the exchange term $V_{ex1}(\mathbf{r})$ can be expressed in terms of polar coordinates as:

$$\begin{aligned} V_{ex1}(\mathbf{r}) &= \int_0^\infty \cancel{r'^2}\mathrm{d}r' \int_0^\pi \sin\theta\,\mathrm{d}\theta \int_0^{2\pi} \mathrm{d}\varphi \\ &\times \frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\left(\cancel{r'^{-2}}|u_{1s}(r')|^2 + 2\cancel{r'^{-2}}|u_{2s}(r')|^2\right)\underbrace{Y_0^0(\Omega)|^2}_{4\pi} \end{aligned}$$

The integrals over angular variables can be simplified to

$$\begin{aligned} \int_0^\pi \sin\theta\,\mathrm{d}\theta \int_0^{2\pi} \mathrm{d}\varphi \frac{1}{|\mathbf{r}-\mathbf{r}'|} &= 2\pi \int_0^\pi \sum_{l=0}^{\infty} \frac{r_m^l}{r_M^l} P_l(\cos\theta)\sin\theta\,\mathrm{d}\theta \\ &= -2\pi \sum_{l=0}^{\infty} \frac{r_m^l}{r_M^l} \int_1^{-1} P_l(\eta)\mathrm{d}\eta \\ &= 2\pi \sum_{l=0}^{\infty} \frac{r_m^l}{r_M^l} \int_{-1}^{1} P_l(\eta)\mathrm{d}\eta \\ &= 2\pi \sum_{l=0}^{\infty} \frac{r_m^l}{r_M^l} 2\delta_{0l} \\ &= \frac{4\pi}{r_M}, \end{aligned}$$

where we have used

$$\eta = \cos\theta \Rightarrow \mathrm{d}\eta = -\sin\theta\,\mathrm{d}\theta.$$

Using this result we obtain

$$V_{C1}(\mathbf{r}) = e^2\left[\int_0^r \frac{\mathrm{d}r'}{r} + \int_r^\infty \frac{\mathrm{d}r'}{r'}\right]\left(|u_{1s}(r')|^2 + 2|u_{2s}(r')|^2\right) = V_{C1}(r)$$

and similarly

$$V_{C3}(\mathbf{r}) = e^2\left[\int_0^r \frac{\mathrm{d}r'}{r} + \int_r^\infty \frac{\mathrm{d}r'}{r'}\right]\left(2|u_{1s}(r')|^2 + |u_{2s}(r')|^2\right) = V_{C3}(r)$$

Then

$$V_{ex1}(\mathbf{r}) = -e^2\left[\int_0^r \frac{\mathrm{d}r'}{r} + \int_r^\infty \frac{\mathrm{d}r'}{r'}\right] u_{1s}^*(r')u_{2s}(r') = V_{ex1}(r) = V_{ex3}^*(r)$$

The Laplacian in polar coordinates for $l = 0$ takes the form

$$\nabla^2 = \frac{1}{r}\frac{\mathrm{d}^2}{\mathrm{d}r^2}r - \cancel{\frac{l(l+1)}{r^2}} = \frac{1}{r}\frac{\mathrm{d}^2}{\mathrm{d}r^2}r$$

which also depends only on r. This concludes the proof because all other terms depend only on r as well.

d) Discuss qualitatively the neutral Be atom in an excited state.

Answer: In the excited atom single electron can occupy an energy level so that its spin should not necessarily be opposite to some other. An example can be $1s2s2p3s$ with spin projections identical for all electrons. This will increase the number of nonzero terms in the equations making them more complicated.