Prof. Stephan Fritzsche
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— Advanced Quantum Theory —

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Winter Term

Home Work (7)

Task 1: Matrix Elements of Slater Determinants (3 Points)

Assume that the ground state of Li can be described by a single Slater determinant

$$\psi = \frac{1}{\sqrt{3!}} \begin{vmatrix} \phi_{1s}\chi_{+1/2}(1) & \phi_{1s}\chi_{+1/2}(2) & \phi_{1s}\chi_{+1/2}(3) \\ \phi_{1s}\chi_{-1/2}(1) & \phi_{1s}\chi_{-1/2}(2) & \phi_{1s}\chi_{-1/2}(3) \\ \phi_{2s}\chi_{+1/2}(1) & \phi_{2s}\chi_{+1/2}(2) & \phi_{2s}\chi_{+1/2}(3) \end{vmatrix} .$$

Here, for example, $\phi_{1s}\chi_{m_s}(1)$ is a spin-orbital of electron 1, while $\phi_{1s}(\mathbf{r}_1)$ is a spatial orbital and χ_{m_s} is a spin-1/2 eigenfunction with the spin quantum number m_s. The Hamiltinian for Li is given by

$$\hat{H} = \sum_{i=1}^{3} \hat{h}(i) + \sum_{i<j}^{3} \frac{2}{r_{ij}} .$$

The term $\hat{h}(i) = -\nabla_i^2/2 - Z/r_i$ is a sum of the kinetic energy and potential energy for each electron in the Coulomb field of a nucleus of charge $Z = 3$. The term with $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ in the denominator is the electrostatic repulsion between the two electrons at $\mathbf{r}_i$ and $\mathbf{r}_j$; the sum is taken over all electrons with $j > i$ to avoid double counting. The I, J, and K integrals are defined by

$$I(i) = \left\langle i \left| \hat{h} \right| i \right\rangle ,$$
$$J(i,j) = \left\langle ij \left| \frac{1}{r_{12}} \right| ij \right\rangle ,$$
$$K(i,j) = \left\langle ij \left| \frac{1}{r_{12}} \right| ji \right\rangle .$$

Using the Condon-Slater rules, derive an expression for the energy $E = \left\langle \psi \left| \hat{H} \right| \psi \right\rangle$ in terms of the I, J, and K integrals.

Task 2: Electron-Electron Interaction (2 Points)

The Legendre polynomials $P_l(w)$ of degree l is defined by the relation

$$(1 - 2sw + s^2)^{-1/2} = \sum_{l=0}^{\infty} P_l(w) s^l , \quad |s| < 1 .$$

Two coordinate vectors $\mathbf{r}_1$ and $\mathbf{r}_2$, with spherical coordinates $(r_1,\, \theta_1,\, \phi_1)$ and $(r_2,\, \theta_2,\, \phi_2)$, respectively, have an angle γ between them: $\cos(\gamma) = \cos(\theta_1)\cos(\theta_2) + \sin(\theta_1)\sin(\theta_2)\cos(\phi_1 - \phi_2)$. The addition

theorem expresses a Legendre polynomial of the order l in the angle γ in terms of products of the spherical harmonics of the angles $(\theta_1,\, \phi_1)$ and $(\theta_2,\, \phi_2)$:

$$P_l(\cos(\gamma)) = \frac{4\pi}{2l+1} \sum_{m=-l}^{l} Y_{lm}^*(\theta_1,\, \phi_1) Y_{lm}(\theta_2,\, \phi_2)\,.$$

Use the definition of Legendre polynomials and the addition theorem to show that the electron-electron repulsion term may be written as

$$\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{4\pi}{2l+1} \frac{(r_<)^l}{(r_>)^{l+1}} Y_{lm}^*(\theta_1,\, \phi_1) Y_{lm}(\theta_2,\, \phi_2)\,.$$

where

$$r_> = r_1 \text{ and } r_< = r_2 \quad \text{for } r_1 > r_2\,,$$

and

$$r_> = r_2 \text{ and } r_< = r_1 \quad \text{for } r_2 > r_1\,,$$

Task 3: Helium Coulomb and Exchange Integrals (3 Points)

a) Show that for the excited states $1s n\ell$ of helium, the energy in first order perturbation theory is given by

$$E^{(1)} = -\frac{1}{2}\left(1 + \frac{1}{n^2}\right) + J_{n\ell} \pm K_{n\ell}$$

where the coulomb $J_{n\ell}$ and exchange integrals $K_{n\ell}$ are defined as

$$J_{nl} = \left\langle \phi_{100}\phi_{n\ell m} \middle| \frac{1}{r_{12}} \middle| \phi_{100}\phi_{n\ell m} \right\rangle \qquad K_{nl} = \left\langle \phi_{100}\phi_{n\ell m} \middle| \frac{1}{r_{12}} \middle| \phi_{n\ell m}\phi_{100} \right\rangle$$

b) Use the result from the previous task to show that the Coulomb and exchange integrals are given by the following expressions

$$J_{n\ell} = \int \mathrm{d}r_1 \mathrm{d}r_2 r_1^2 r_2^2 R_{10}(r_1)^2 R_{n\ell}(r_2)^2 \frac{1}{r_>}$$
$$K_{n\ell} = \frac{1}{2\ell+1} \int \mathrm{d}r_1 \mathrm{d}r_2 r_1^2 r_2^2 R_{n\ell}(r_1) R_{10}(r_1) \frac{r_<^\ell}{r_>^{\ell+1}} R_{n\ell}(r_2) R_{10}(r_2)$$

Task 4: Helium Perturbation Theory (4 Points)

Calculate the energies for the $1s2s\ {}^1S$, $1s2p\ {}^1P$, $1s2s\ {}^3S$ and $1s2p\ {}^3P$ states of helium in first-order perturbation theory.

Hint: Do not try to solve all integrals by hand.

The integrals evaluated in the previous task were formulated in atomic units, such that energies are expressed in units of the Hartree energy $1\,\mathrm{au} = 2R = 27.211\,\mathrm{eV}$. Therefore, they need to be multiplied with a factor $e^2/(4\pi\epsilon_0)$ to obtain results in Si units (together with the corresponding wave functions).