

DYLAN J. TEMPLES: SOLUTION SET THREE

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1 Electron in Short Range Potential.

Consider an electron bound to an attractive short-ranged potential that can be approximated by a delta function with a strength given by $V(x) = -e^2\delta(x)$, where e is the electron charge.

1.1 Estimation of Ground State Energy.

Obtain a best estimate for the ground state energy assuming a variational wave function of the form, $\psi_\mu(x) = \psi_0 e^{-\mu x^2/2}$. Express your result in units of the Rydberg, R_H .

For ψ_μ to be properly normalized, we enforce

$$1 = \int |\psi_\mu(x)|^2 dx = |\psi_0|^2 \int_{-\infty}^{\infty} e^{-\mu x^2} dx = \left(\frac{\pi}{\mu}\right)^{1/2}, \quad (1)$$

which gives $|\psi_0| = (\mu/\pi)^{1/4}$. The variational energy is given by

$$E(\mu) = \langle \psi_\mu | \hat{\mathcal{H}} | \psi_\mu \rangle = -\frac{\hbar^2}{2m} \langle \psi_\mu | \hat{\mathbf{p}}^2 | \psi_\mu \rangle - e^2 \langle \psi_\mu | \hat{V} | \psi_\mu \rangle. \quad (2)$$

The kinetic energy term can be expressed in the coordinate basis as

$$-\frac{\hbar^2}{2m} \langle \psi_\mu | \hat{\mathbf{p}}^2 | \psi_\mu \rangle = -\frac{\hbar^2}{2m} |\psi_0|^2 \int_{-\infty}^{\infty} e^{-\mu x^2/2} \frac{\partial^2}{\partial x^2} \left(e^{-\mu x^2/2} \right) dx. \quad (3)$$

The second derivative is

$$\frac{\partial^2}{\partial x^2} \left(e^{-\mu x^2/2} \right) = -\mu \frac{\partial}{\partial x} \left(x e^{-\mu x^2/2} \right) = \mu^2 x^2 e^{-\mu x^2/2} - \mu e^{-\mu x^2/2} = \mu (\mu x^2 - 1) e^{-\mu x^2/2}, \quad (4)$$

so the integral in the kinetic energy term is

$$\mu \int_{-\infty}^{\infty} (\mu x^2 - 1) e^{-\mu x^2} dx = -\frac{1}{2} \sqrt{\pi \mu}, \quad (5)$$

so the kinetic term contributes

$$\langle \psi_0 | \hat{T} | \psi_0 \rangle = -\frac{\hbar^2}{2m} \left(\frac{\mu}{\pi}\right)^{1/2} \left(-\frac{1}{2} \sqrt{\pi \mu}\right) = \frac{\hbar^2 \mu}{4m}. \quad (6)$$

The contribution to the energy from the potential term is

$$-e^2 \langle \psi_\mu | \hat{V} | \psi_\mu \rangle = -e^2 |\psi_0|^2 \int_{-\infty}^{\infty} e^{-\mu x^2} \delta(x) dx = -e^2 \left(\frac{\mu}{\pi}\right)^{1/2}. \quad (7)$$

Inserting the results into Equation 2 yields

$$E(\mu) = \frac{\mu \hbar^2}{4m} - e^2 \sqrt{\frac{\mu}{\pi}}, \quad (8)$$

which for the ground state is minimized with respect to the variational parameter μ :

$$0 = \frac{\partial}{\partial \mu} \left(\frac{\mu \hbar^2}{4m} - e^2 \sqrt{\frac{\mu}{\pi}} \right) = \frac{\hbar^2}{4m} - \frac{e^2}{2\sqrt{\pi \mu}}, \quad (9)$$

so the value of μ which minimizes the ground state energy is

$$\mu = \left(\frac{e^2}{2\sqrt{\pi}} \frac{4m}{\hbar^2} \right)^2 = \frac{4}{\pi} \left(\frac{me^2}{\hbar^2} \right)^2 = \frac{4}{\pi} \frac{1}{a_0^2}, \quad (10)$$

where $a_0 = \hbar^2/me^2$ is the Bohr radius. Inserting this into the variational energy, we obtain

$$E_0 = \frac{\hbar^2}{4m} \frac{4}{\pi a_0^2} - \frac{e^2}{\sqrt{\pi}} \sqrt{\frac{4}{\pi a_0^2}} = \frac{1}{\pi} \frac{e^2}{a_0} - \frac{2}{\pi} \frac{e^2}{a_0}, \quad (11)$$

using the definition of the Rydberg, $R_H = e^2/2a_0 = me^4/2\hbar^2$, we have

$$E_0 = \frac{2}{2\pi} \frac{e^2}{a_0} (1 - 2) = -\frac{2}{\pi} R_H = -0.636 R_H. \quad (12)$$

1.2 Exact Ground State Energy.

Solve the Schrödinger equation for the ground state wave function and calculate the exact result for the ground state energy in terms of the Rydberg.

The exact ground state energy \mathcal{E}_0 can be found using the Schrödinger equation:

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi_0(x) - e^2 \delta(x) \psi_0(x) = \mathcal{E}_0 \psi_0(x) \quad \Rightarrow \quad \psi'' = -\frac{2m}{\hbar^2} (\mathcal{E}_0 - e^2 \delta(x)) \psi, \quad (13)$$

where primes denote derivatives with respect to the coordinate x . At every point excluding $x = 0$, the term with the delta function vanishes, and if we define $\kappa = \sqrt{-2m\mathcal{E}_0/\hbar^2}$ (which is positive because for bound states $\mathcal{E}_0 < 0$), we are left with the differential equation

$$\psi'' = \kappa^2 \psi \quad x \neq 0, \quad (14)$$

which has solutions

$$\psi(x) = \begin{cases} Ae^{-\kappa x} & x > 0 \\ Ae^{\kappa x} & x < 0 \end{cases}, \quad (15)$$

where we have enforced continuity at $x = 0$ by using same the coefficient A for the wave functions in both regions. Normalization gives us $|A|^2 = \pm 2\kappa$, we can select the positive value, so that $A \in \mathbb{R}$. Due to the presence of the delta function, there is a discontinuity in the first derivative at $x = 0$. Consider integrating the Schrödinger equation over an infinitesimal region around the origin:

$$\int_{-\epsilon}^{+\epsilon} \frac{\partial^2 \psi}{\partial x^2} = -\frac{2m}{\hbar^2} \int_{-\epsilon}^{+\epsilon} (e^2 \delta(x) + \mathcal{E}_0) \psi. \quad (16)$$

In the limit $\epsilon \rightarrow 0$, the integral of the regular quantity $\kappa^2 \psi$ must vanish because the range of integration is infinitesimal. This is not the case for the delta function, which is “infinite” at the origin. Carrying out the integration of the second derivative on the right-hand side, and taking the limit $\epsilon \rightarrow 0$, we obtain

$$\frac{\partial \psi}{\partial x} \Big|_{x=0+} - \frac{\partial \psi}{\partial x} \Big|_{x=0-} = -\frac{2m}{\hbar^2} \int_{-\epsilon}^{+\epsilon} e^2 \delta(x) \psi = -\frac{2m}{\hbar^2} e^2 \psi(0). \quad (17)$$

Therefore, the condition on the continuity of the first derivative at $x = 0$ gives

$$-A\kappa e^{-kx} \Big|_{x=0^+} - A\kappa e^{kx} \Big|_{x=0^-} = -\frac{2m}{\hbar^2} e^2 \psi(0) \quad (18)$$

$$-2\kappa = -\frac{2m}{\hbar^2} e^2, \quad (19)$$

using $\psi(0) = A$, we obtain the relation $\kappa = me^2/\hbar^2$. Setting this equivalent to the definition of κ^2 , we obtain

$$\left(\frac{me^2}{\hbar^2}\right)^2 = -\frac{2m\mathcal{E}_0}{\hbar^2} \Rightarrow \mathcal{E}_0 = -\frac{\hbar^2}{2m} \frac{m^2 e^4}{\hbar^4} = -\frac{me^4}{2\hbar^2} = -R_H. \quad (20)$$

2 Two Electron Atoms: Coulomb Repulsion.

Two identical particles of spin $s = 1/2$ are confined to a cubical box whose sides are $d = 10^{-8}$ cm in length. The particles are attracted to one another via a potential of strength $V_0 = 10^{-3}$ eV whenever they are within a distance of $a = 10^{-10}$ cm of one another. Calculate the ground state energy and wave function of the particles assuming they each have a mass, m , equal to that of the electron. Express your result for the ground state energy in terms of \hbar, m, V_0, a, d . Does the ground state have a definite total spin? If so what is the total spin? If not what are the probabilities of measuring the allowed values of total spin S in the two-particle ground state? Hint: pay attention at the beginning to the length scales involved in this problem.

The length scale of the interaction is two orders of magnitude smaller than the length scale which defines the volume. Therefore the volume in which the fermions can interact is a factor of 10^6 smaller than the total volume they occupy¹. For this reason, the potential

$$\hat{V} = V_0 \Theta \{a - |\mathbf{r}_1 - \mathbf{r}_2|\} , \quad (21)$$

where $\Theta(x)$ is the Heaviside theta function, can be approximated as

$$\hat{V} = V_0 \mathcal{V} \delta^3 \{\mathbf{r}_1 - \mathbf{r}_2\} = \frac{4\pi}{3} a^3 V_0 \delta^3 \{\mathbf{r}_1 - \mathbf{r}_2\} , \quad (22)$$

where we have picked up a factor of the volume for approximating the Heaviside function as a delta function (really the three dimensional delta is three one dimensional deltas each with a factor of the length scale on which the Heaviside is nonzero). This is needed because the Heaviside is dimensionless and the delta function has dimensions which are the inverse of its argument. We have selected the length scale a because this determines the volume on which the interaction occurs (where the Heaviside function is nonzero) so the strength of the perturbation will depend on the scale of the interaction. Additionally, the amplitude of the potential is small, and due to the relative size of the interaction volume compared to the total volume, the particles have a much lower probability of being within a of each other than being separated by a distance greater than a . For these reasons we may treat the potential as a perturbation. The unperturbed wave function for a single particle is simply that of a infinite cubic well, with the conditions that $\psi(x_i = 0) = \psi(x_i = d) = 0$, where x_i are the Cartesian coordinates, with the origin at one corner of the box. The solutions to the Schrödinger equation are harmonic, but we may ignore the cosine term because it does not satisfy the boundary conditions, so

$$\psi_{nmp}(\mathbf{r}) = \left(\frac{2}{d}\right)^{3/2} \sin\left(\frac{n\pi}{d}x\right) \sin\left(\frac{m\pi}{d}y\right) \sin\left(\frac{p\pi}{d}z\right) , \quad (23)$$

with energies

$$E_{nmp} = \frac{\hbar^2 \pi^2}{2md^2} (n^2 + m^2 + z^2) \equiv \frac{\hbar^2 \pi^2}{2md^2} N^2 , \quad (24)$$

which is $\frac{1}{2}(N+1)(N+2)$ fold degenerate. If the box now has two electrons, the wave function can be represented as a product of a two-fermion spatial state $|\phi\rangle$ and a two-fermion spin state $|\chi\rangle$:

$$|\Psi\rangle = |\phi\rangle \otimes |\chi\rangle = \frac{1}{\sqrt{2}} (|nmp\rangle_1 \otimes |n'm'p'\rangle_2 - P_{12}(S) |nmp\rangle_2 \otimes |n'm'p'\rangle_1) \otimes |S, M_S\rangle , \quad (25)$$

¹The total volume is $(10^{-8})^3 \text{ cm}^3 = 10^{-24} \text{ cm}^3$, while the interaction volume is $(10^{-10})^3 \text{ cm}^3 = 10^{-30} \text{ cm}^3$, and thus the ratio is $\mathcal{V}_{\text{int}}/\mathcal{V}_{\text{tot}} = 10^{-6}$.

where the subscripts denote the particle index, $P_{12}(S)$ is the parity exchange operator, defined by

$$P_{12}(S) = \begin{cases} +1 & S = 1 \\ -1 & S = 0 \end{cases}, \quad (26)$$

and $|S, M_S\rangle$ denotes the two-fermion spin states:

$$\text{triplet: } \begin{cases} |1, 1\rangle & = |\uparrow\rangle_1 \otimes |\uparrow\rangle_2 \\ |1, 0\rangle & = \frac{1}{\sqrt{2}} (|\uparrow\rangle_1 \otimes |\downarrow\rangle_2 + |\downarrow\rangle_1 \otimes |\uparrow\rangle_2) \\ |1, -1\rangle & = |\downarrow\rangle_1 \otimes |\downarrow\rangle_2 \end{cases} \quad (27)$$

$$\text{singlet: } \begin{cases} |0, 0\rangle & = \frac{1}{\sqrt{2}} (|\uparrow\rangle_1 \otimes |\downarrow\rangle_2 - |\downarrow\rangle_1 \otimes |\uparrow\rangle_2) \end{cases} \quad (28)$$

Note the symmetry requirements imposed by the spin states: if the fermions are in the singlet state ($S = 0$), which is antisymmetric, the spatial wave function must be symmetric to ensure total antisymmetry of the wave function, which is ensured by the definition of the parity exchange operator. Conversely, when the spin state is symmetric (triplet, $S = 1$) the spatial part of the wave function is antisymmetric due to the parity exchange operator. The product states $|\Psi\rangle$ are eigenstates of the Hamiltonian, with an energy spectrum

$$E_{nmpn'm'p'} = \frac{\hbar^2 \pi^2}{2md^2} (n^2 + m^2 + z^2) + \frac{\hbar^2 \pi^2}{2md^2} ((n')^2 + (m')^2 + (p')^2) = \frac{\hbar^2 \pi^2}{2md^2} (N^2 + (N')^2), \quad (29)$$

with $N^2 = n^2 + m^2 + p^2$ and $N'^2 = (n')^2 + (m')^2 + (p')^2$ (note that N and N' are not necessarily integers). The ground state of the single-fermion system is simply E_{111} because for any index $\{n, m, p\} = 0$, the wave function is zero due to it being a product of sines. Similarly, we see that the lowest energy state, for which the wave function is nonzero, of the two-fermion system is $|nmp\rangle = |n'm'p'\rangle = |111\rangle$. This state is allowed only for $S = 0$ due to parity, and as such we may write the ground state $|\Psi_0\rangle$ of the two-fermion system as

$$|\Psi\rangle = \frac{1}{\sqrt{2}} (|111\rangle_1 \otimes |111\rangle_2 - (-1) |111\rangle_2 \otimes |111\rangle_1) \otimes |0, 0\rangle \quad (30)$$

$$= \frac{2}{\sqrt{2}} |111\rangle_1 \otimes |111\rangle_2 \otimes \frac{1}{\sqrt{2}} (|\uparrow\rangle_1 \otimes |\downarrow\rangle_2 - |\downarrow\rangle_1 \otimes |\uparrow\rangle_2) \quad (31)$$

$$\equiv \{ |111\rangle_1 \otimes |111\rangle_2 \} \otimes (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle). \quad (32)$$

In the coordinate basis this is

$$\langle \mathbf{r}_1 \mathbf{r}_2 | \Psi_0 \rangle = \{ \langle \mathbf{r}_1 | 111 \rangle \otimes \langle \mathbf{r}_2 | 111 \rangle \} \otimes (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) \quad (33)$$

$$\Psi_0(\mathbf{r}_1, \mathbf{r}_2) = \left(\frac{2}{d}\right)^3 \sin\left(\frac{\pi}{d}x_1\right) \sin\left(\frac{\pi}{d}y_1\right) \sin\left(\frac{\pi}{d}z_1\right) \sin\left(\frac{\pi}{d}x_2\right) \sin\left(\frac{\pi}{d}y_2\right) \sin\left(\frac{\pi}{d}z_2\right) \otimes |0, 0\rangle. \quad (34)$$

The energy of the unperturbed ground state has $N^2 = (N')^2 = 3$, and therefore

$$E_0^{(0)} = 3 \frac{\hbar^2 \pi^2}{md^2}. \quad (35)$$

The first-order correction to the energy of the ground state due to the perturbation \hat{V} is

$$\Delta E_0^{(1)}/\mathcal{V} = \langle \Psi_0 | \hat{V} / \mathcal{V} | \Psi_0 \rangle = V_0 \langle \Psi_0 | \delta^3(\mathbf{r}_1 - \mathbf{r}_2) | \Psi_0 \rangle = V_0 \langle \phi_0 | \delta^3(\mathbf{r}_1 - \mathbf{r}_2) | \phi_0 \rangle \cdot \langle 0, 0 | \mathbb{1} | 0, 0 \rangle, \quad (36)$$

and the inner product of the spin states does not contribute to the energy shift. In the coordinate basis, this matrix element is

$$\begin{aligned}\Delta E_0^{(1)}/\mathcal{V} &= V_0 \langle \phi_0 | \delta^3(\mathbf{r}_1 - \mathbf{r}_2) | \phi_0 \rangle \\ &= a^3 V_0 \left(\frac{2}{d} \right)^6 \int d^3 \mathbf{r}_1 \int d^3 \mathbf{r}_2 \delta^3(\mathbf{r}_1 - \mathbf{r}_2) \sin^2(\bar{x}_1) \sin^2(\bar{y}_1) \sin^2(\bar{z}_1) \sin^2(\bar{x}_2) \sin^2(\bar{y}_2) \sin^2(\bar{z}_2),\end{aligned}$$

where $\bar{x}_i = \pi x_i/2$, and likewise for y and z . Performing the first integral over \mathbf{r}_2 just selects the value of the function at $\mathbf{r}_2 = \mathbf{r}_1 \equiv \mathbf{r}$:

$$\begin{aligned}\frac{\Delta E_0^{(1)}}{a^3 V_0} &= \left(\frac{2}{d} \right)^6 \int d^3 \mathbf{r}_1 \sin^2(\bar{x}_1) \sin^2(\bar{y}_1) \sin^2(\bar{z}_1) \int d^3 \mathbf{r}_2 \delta^3(\mathbf{r}_1 - \mathbf{r}_2) \sin^2(\bar{x}_2) \sin^2(\bar{y}_2) \sin^2(\bar{z}_2) \\ &= \left(\frac{2}{d} \right)^6 \int d^3 \mathbf{r}_1 \sin^2(\bar{x}_1) \sin^2(\bar{y}_1) \sin^2(\bar{z}_1) \sin^2(\bar{x}_1) \sin^2(\bar{y}_1) \sin^2(\bar{z}_1) \\ &= \left(\frac{2}{d} \right)^6 \int_0^d dx \int_0^d dy \int_0^d dz \sin^4\left(\frac{n\pi}{d}x\right) \sin^4\left(\frac{n\pi}{d}y\right) \sin^4\left(\frac{n\pi}{d}z\right) \\ &= \left(\frac{2}{d} \right)^6 \left\{ \int_0^d dx \sin^4\left(\frac{n\pi}{d}x\right) \right\}^3 = \left(\frac{2}{d} \right)^6 \left(\frac{3d}{8} \right)^3 = \frac{27}{8d^3}.\end{aligned}$$

The ground state energy of the two-fermion system, to first-order, is

$$E_0^{(1)} = E_0^{(0)} + \Delta E_0^{(1)} = 3 \frac{\hbar^2 \pi^2}{md^2} + \frac{27}{8} V_0 \frac{4\pi}{3} \left(\frac{a}{d} \right)^3 \quad (37)$$

The numeric value of the first-order energy shift due to perturbation is

$$\Delta E_0^{(1)} = \frac{27}{8} V_0 \frac{4\pi}{3} \left(\frac{a}{d} \right)^3 = \frac{27}{8} 10^{-3} \frac{4\pi}{3} (10^{-2})^3 \text{ eV} = \frac{9\pi}{2 \times 10^9} \text{ eV} = 1.41 \times 10^{-8} \text{ eV}. \quad (38)$$

The unperturbed ground state energy is

$$E_0^{(0)} = 3 \frac{\hbar^2 \pi^2}{md^2} = \frac{194.885 \text{ eV}^2 \cdot \text{s}^2}{m \text{ cm}^2}, \quad (39)$$

where m is measured in grams. If we measure m in eV, the unperturbed ground state energy is

$$E_0^{(0)} = \frac{1.216 \times 10^{14}}{m} \text{ eV}^2, \quad (40)$$

inserting the electron mass yields

$$E_0^{(0)} = \frac{1.216 \times 10^{14}}{511 \times 10^3} \text{ eV} = 2.38 \times 10^8 \text{ eV}. \quad (41)$$

3 Excited States of Helium.

Consider excited states of Helium with the configuration $[1s\ 2s]$ and $[1s\ 2p]$, in which one electron is in the $(1s)$ single-electron orbital and the other electron is in an excited $(2s)$ or $(2p)$ orbital. The energy calculated in first-order perturbation theory in the electron-electron interaction of such a state can be written as

$$E(2, \ell, m_\ell; S) = -5R_H + \Delta_d(2, \ell, m_\ell) - P_{12}(S)\Delta_{\text{ex}}(2, \ell, m_\ell), \quad (42)$$

where $R_H = e^2/2a_0 = 13.6$ eV is the Rydberg, S is the total spin and $P_{12}(S = \{1, 0\}) = \{+1, -1\}$.

Technical Hint.

To calculate the direct and exchange terms in Eq. 42 express the the direct contribution to the Coulomb energy in terms of the Fourier transforms of the probability densities for $1s$ and $2s$ Hydrogenic states of the electron,

$$\rho_{1s}(\mathbf{q}) = \int d^3r e^{-i\mathbf{q}\cdot\mathbf{r}} |\psi_{1s}(r)|^2 \quad (43)$$

$$\rho_{2s}(\mathbf{q}) = \int d^3r e^{-i\mathbf{q}\cdot\mathbf{r}} |\psi_{2s}(r)|^2, \quad (44)$$

and the Fourier transform of the Coulomb interaction,

$$\int d^3r e^{-i\mathbf{q}\cdot\mathbf{r}} \frac{e^2}{|\mathbf{r}|} = \frac{4\pi e^2}{q^2}. \quad (45)$$

For the exchange term you need the Fourier transform of the “overlap”

$$\rho_{\text{ex}} = \int d^3r e^{-i\mathbf{q}\cdot\mathbf{r}} \psi_{1s}(r)\psi_{2s}(r). \quad (46)$$

Scale the Coulomb and exchange energies in units of e^2/a , where $a = a_0/Z$. The coefficient is now a dimensionless integral. Use the results of Exercise 1 to evaluate the resulting direct and exchange contributions for the matrix elements of the Coulomb interaction.

3.1 Direct and Exchange Energy Integrals.

Write down the direct and exchange integrals, Δ_d and Δ_{ex} , for the $[1s\ 2s]$ and $[1s\ 2p]$ states.

The first-order energy shift is given by

$$\Delta E(n, \ell, m_\ell; S) = \langle NLM_L; S | \hat{V}_{ee} | NLM_L; S \rangle = \Delta_d(n, \ell, m_\ell) - P_{12}(S)\Delta_{\text{ex}}(n, \ell, m_\ell), \quad (47)$$

where \hat{V}_{ee} is the Coulomb potential between the two electrons, and the state vectors are defined to be

$$|NLM_L; S\rangle = \frac{1}{\sqrt{2}} \left(|1s\rangle \otimes |nlm_\ell\rangle - \hat{P}_{12}(S) |nlm_\ell\rangle \otimes |1s\rangle \right), \quad (48)$$

which is a linear combination of the two electrons in each possible state (the ground state $1s$, and an excited state) which obeys the necessary symmetry requirement determined by the total spin state of the two-electron system. The matrix element in Equation 47 results in terms of the form

$$\frac{1}{2} \langle 1s; nlm_\ell | \hat{V}_{ee} | 1s; nlm_\ell \rangle + \frac{1}{2} \langle nlm_\ell; 1s | \hat{V}_{ee} | nlm_\ell; 1s \rangle \quad (49)$$

$$\frac{1}{2} \langle 1s; nlm_\ell | \hat{V}_{ee} | nlm_\ell; 1s \rangle + \frac{1}{2} \langle nlm_\ell; 1s | \hat{V}_{ee} | 1s; nlm_\ell \rangle, \quad (50)$$

which are the direct and exchange contributions, respectively. In the coordinate basis, these matrix elements can be expressed as the integrals:

$$\Delta_d(n, \ell, m_\ell) = \int d^3r_1 \int d^3r_2 |\psi_{100}(\mathbf{r}_1)|^2 \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} |\psi_{n\ell m_\ell}(\mathbf{r}_2)|^2 \quad (51)$$

$$\Delta_{\text{ex}}(n, \ell, m_\ell) = \int d^3r_1 \int d^3r_2 \Re \left\{ \psi_{100}^*(\mathbf{r}_1) \psi_{n\ell m_\ell}(\mathbf{r}_2) \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \psi_{n\ell m_\ell}^*(\mathbf{r}_1) \psi_{100}(\mathbf{r}_2) \right\}, \quad (52)$$

where $\psi_{n\ell m_\ell}(\mathbf{r})$ are the single-electron wave functions for Hydrogenic atoms:

$$|1s\rangle = |100\rangle = \psi_{100}(\mathbf{r}) = \sqrt{\frac{Z^3}{\pi a_0^3}} e^{-Zr/a_0} \quad (53)$$

$$|2s\rangle = |200\rangle = \psi_{200}(\mathbf{r}) = \sqrt{\frac{Z^3}{32\pi a_0^3}} e^{-Zr/2a_0} \left(2 - \frac{Zr}{a_0} \right) \quad (54)$$

$$|2p_0\rangle = |210\rangle = \psi_{210}(\mathbf{r}) = \sqrt{\frac{Z^3}{32\pi a_0^3}} e^{-Zr/2a_0} \frac{Zr}{a_0} \cos\theta \quad (55)$$

$$|2p_{\pm 1}\rangle = |21 \pm 1\rangle = \psi_{21 \pm 1}(\mathbf{r}) = \frac{2}{\sqrt{2}} \sqrt{\frac{Z^3}{32\pi a_0^3}} e^{-Zr/2a_0} \frac{Zr}{a_0} \sin\theta e^{\pm i\phi}, \quad (56)$$

for helium, we have $Z = 2$. Using the technical hint and Equations 51 and 52 we can write the direct and exchange integrals in Fourier q -space²:

$$\Delta_d(n, \ell, m_\ell) = \int \frac{d^3q}{(2\pi)^3} \rho_{100}(\mathbf{q}) \frac{4\pi e^2}{q^2} \rho_{n\ell m_\ell}(\mathbf{q}) \quad (57)$$

$$\Delta_{\text{ex}}(n, \ell, m_\ell) = \int \frac{d^3q}{(2\pi)^3} |\rho_{\text{ex}}(\mathbf{q})|^2 \frac{4\pi e^2}{q^2}, \quad (58)$$

with

$$\rho_{\text{ex}}(\mathbf{q}) = \int d^3r e^{-i\mathbf{q}\cdot\mathbf{r}} \psi_{100}(r) \psi_{n\ell m_\ell}(r). \quad (59)$$

For the $[1s\ 2s]$ state we have $|n\ell m_\ell\rangle \rightarrow |200\rangle$ and for $[1s\ 2p]$ we have $|n\ell m_\ell\rangle \rightarrow |21m_\ell\rangle$.

3.2 Electron-Electron Interaction Energies.

Calculate to first-order in the electron-electron interaction the energies of the “ortho” (spin-triplet, 2^3S) and “para” (spin-singlet, 2^1S) excited $[1s\ 2s]$ states of Helium. Compare the perturbation theory results with the experimentally determined level structure of Helium. See for example tabulations by the NIST at the URL:

<http://physics.nist.gov/PhysRefData/Handbook/Tables/heliumtable5.htm>.

To determine the first order energy shifts of the $[1s\ 2s]$ state, we must calculate $\rho_{100}(\mathbf{q})$, $\rho_{200}(\mathbf{q})$, and

$$\rho_{\text{ex}}(\mathbf{q}) = \int d^3r e^{-i\mathbf{q}\cdot\mathbf{r}} \psi_{100}(r) \psi_{200}(r). \quad (60)$$

²Note that for the $[1s\ 2s]$ state, both wave functions are entirely real, so taking the real part in the exchange integral leaves the integrand unchanged.

The first Fourier density is

$$\rho_{1s}(\mathbf{q}) = \int d^3r e^{-i\mathbf{q}\cdot\mathbf{r}} |\psi_{1s}(r)|^2 = \int d^3r e^{-i\mathbf{q}\cdot\mathbf{r}} \left| \sqrt{\frac{Z^3}{\pi a_0^3}} e^{-Zr/a_0} \right|^2 \quad (61)$$

$$= \frac{Z^3}{\pi a_0^3} \int d^3r e^{-i\mathbf{q}\cdot\mathbf{r}} e^{-2Zr/a_0} = \frac{Z^3}{\pi a_0^3} \int_0^{2\pi} d\phi \int_{-1}^1 d(\cos\theta) \int_0^\infty r^2 dr e^{-iqr \cos\theta} e^{-2Zr/a_0} \quad (62)$$

$$= \frac{2Z^3}{a_0^3} \int_0^\infty r^2 dr e^{-2Zr/a_0} \int_{-1}^1 d(\cos\theta) e^{-iqr \cos\theta} = \frac{2Z^3}{a_0^3} \int_0^\infty r^2 dr e^{-2Zr/a_0} \frac{2 \sin(qr)}{qr} \quad (63)$$

$$= \frac{4Z^3}{qa_0^3} \int_0^\infty r \sin(qr) e^{-2Zr/a_0} dr = \frac{4Z^3}{qa_0^3} \left(\frac{4a_0^3 q Z}{(a_0^2 q^2 + 4Z^2)^2} \right) \quad (64)$$

$$= \frac{16Z^4}{(a_0^2 q^2 + 4Z^2)^2} = \frac{Z^4}{\left(\frac{a_0^2 q^2}{4} + Z^2\right)^2} = \frac{Z^4}{\left[Z^2 + \left(\frac{a_0 q}{2}\right)^2\right]^2}, \quad (65)$$

and the second is³

$$\rho_{2s}(\mathbf{q}) = \int d^3r e^{-i\mathbf{q}\cdot\mathbf{r}} |\psi_{2s}(r)|^2 = \int d^3r e^{-i\mathbf{q}\cdot\mathbf{r}} \left| \sqrt{\frac{Z^3}{32\pi a_0^3}} e^{-Zr/2a_0} \left(2 - \frac{Zr}{a_0}\right) \right|^2 \quad (66)$$

$$= \frac{Z^3}{32\pi a_0^3} \int d^3r e^{-i\mathbf{q}\cdot\mathbf{r}} e^{-Zr/a_0} \left(2 - \frac{Zr}{a_0}\right)^2 \quad (67)$$

$$= \frac{Z^3}{32\pi a_0^3} \int_0^{2\pi} d\phi \int_{-1}^1 d(\cos\theta) \int_0^\infty r^2 dr e^{-iqr \cos\theta} e^{-Zr/a_0} \left(2 - \frac{Zr}{a_0}\right)^2 \quad (68)$$

$$= \frac{Z^3}{16a_0^3} \int_0^\infty r^2 dr e^{-Zr/a_0} \left(2 - \frac{Zr}{a_0}\right)^2 \int_{-1}^1 d(\cos\theta) e^{-iqr \cos\theta} \quad (69)$$

$$= \frac{Z^3}{16a_0^3} \int_0^\infty r^2 dr e^{-Zr/a_0} \left(2 - \frac{Zr}{a_0}\right)^2 \frac{2 \sin(qr)}{qr} \quad (70)$$

$$= \frac{Z^3}{8qa_0^3} \int_0^\infty r \sin(qr) e^{-Zr/a_0} \left(2 - \frac{Zr}{a_0}\right)^2 dr \quad (71)$$

$$= \frac{Z^3}{8qa_0^3} \int_0^\infty r \sin(qr) e^{-Zr/a_0} \left(\frac{Z^2 r^2}{a_0^2} - 4 \frac{Zr}{a_0} + 4 \right) dr. \quad (72)$$

³Some useful identities:

$$\int_{-1}^1 e^{-iqr x} dx = \frac{2 \sin(qr)}{qr}$$

This splits into three integrals:

$$\int_0^\infty r \sin(qr) e^{-Zr/a_0} \left(\frac{Z^2 r^2}{a_0^2} \right) dr = \frac{Z^2}{a_0^2} \int_0^\infty r^3 \sin(qr) e^{-Zr/a_0} dr \quad (73)$$

$$= \frac{Z^2}{a_0^2} \left(\frac{24a_0^5 q Z (Z^2 - a_0^2 q^2)}{(a_0^2 q^2 + Z^2)^4} \right) \quad (74)$$

$$\int_0^\infty r \sin(qr) e^{-Zr/a_0} \left(-4 \frac{Zr}{a_0} \right) dr = -4 \frac{Z}{a_0} \int_0^\infty r^2 \sin(qr) e^{-Zr/a_0} dr \quad (75)$$

$$= -4 \frac{Z}{a_0} \left(-\frac{2a_0^4 q (a_0^2 q^2 - 3Z^2)}{(a_0^2 q^2 + Z^2)^3} \right) \quad (76)$$

$$\int_0^\infty r \sin(qr) e^{-Zr/a_0} (4) dr = 4 \int_0^\infty r \sin(qr) e^{-Zr/a_0} dr \quad (77)$$

$$= 4 \frac{2a_0^3 q Z}{(a_0^2 q^2 + Z^2)^2} . \quad (78)$$

Summing these, we find

$$\rho_{2s}(\mathbf{q}) = \frac{Z^3}{8q a_0^3} \left\{ \left(\frac{24a_0^3 q Z^3 (Z^2 - a_0^2 q^2)}{(a_0^2 q^2 + Z^2)^4} \right) + \left(\frac{8a_0^3 q Z (a_0^2 q^2 - 3Z^2)}{(a_0^2 q^2 + Z^2)^3} \right) + \frac{8a_0^3 q Z}{(a_0^2 q^2 + Z^2)^2} \right\} \quad (79)$$

$$= \frac{3Z^6 (Z^2 - a_0^2 q^2)}{(a_0^2 q^2 + Z^2)^4} + \frac{Z^4 (a_0^2 q^2 - 3Z^2)}{(a_0^2 q^2 + Z^2)^3} + \frac{Z^4}{(a_0^2 q^2 + Z^2)^2} \quad (80)$$

$$= \frac{3Z^6 (Z^2 - a_0^2 q^2)}{(a_0^2 q^2 + Z^2)^4} + \frac{Z^4 (a_0^2 q^2 - 3Z^2) (a_0^2 q^2 + Z^2)}{(a_0^2 q^2 + Z^2)^4} + \frac{Z^4 (a_0^2 q^2 + Z^2)^2}{(a_0^2 q^2 + Z^2)^4} \quad (81)$$

$$= \frac{2a_0^4 q^4 Z^4 - 3a_0^2 q^2 Z^6 + Z^8}{(a_0^2 q^2 + Z^2)^4} = \frac{Z^4 (a_0^2 q^2 - Z^2) (2a_0^2 q^2 - Z^2)}{(a_0^2 q^2 + Z^2)^4} . \quad (82)$$

The exchange density is given by

$$\rho_{\text{ex}} = \int d^3 r e^{-i\mathbf{q}\cdot\mathbf{r}} \psi_{1s}(r) \psi_{2s}(r) = \int d^3 r e^{-i\mathbf{q}\cdot\mathbf{r}} \sqrt{\frac{Z^3}{\pi a_0^3}} e^{-Zr/a_0} \sqrt{\frac{Z^3}{32\pi a_0^3}} e^{-Zr/2a_0} \left(2 - \frac{Zr}{a_0} \right) \quad (83)$$

$$= \frac{Z^3}{\sqrt{32\pi a_0^3}} \int d^3 r e^{-i\mathbf{q}\cdot\mathbf{r}} e^{-\frac{Z}{a_0}(r+\frac{r}{2})} \left(2 - \frac{Zr}{a_0} \right) , \quad (84)$$

again moving to spherical coordinates, we have

$$\rho_{\text{ex}} = \frac{Z^3}{\sqrt{32\pi a_0^3}} \int_0^{2\pi} d\phi \int_{-1}^1 d(\cos \theta) \int_0^\infty r^2 dr e^{-iqr \cos \theta} e^{-3Zr/2a_0} \left(2 - \frac{Zr}{a_0} \right) \quad (85)$$

$$= \frac{2Z^3}{\sqrt{32\pi a_0^3}} \int_0^\infty r^2 dr e^{-3Zr/2a_0} \left(2 - \frac{Zr}{a_0} \right) \int_{-1}^1 d(\cos \theta) e^{-iqr \cos \theta} \quad (86)$$

$$= \frac{2Z^3}{\sqrt{32\pi a_0^3}} \int_0^\infty r^2 dr e^{-3Zr/2a_0} \left(2 - \frac{Zr}{a_0} \right) \frac{2 \sin(qr)}{qr} \quad (87)$$

$$= \frac{4Z^3}{4\sqrt{2}a_0^3 q} \int_0^\infty r \sin(qr) e^{-3Zr/2a_0} \left(2 - \frac{Zr}{a_0} \right) dr . \quad (88)$$

Separating the integrals yields

$$\rho_{\text{ex}} = \frac{Z^3}{\sqrt{2}a_0^3q} \left(2 \int_0^\infty r \sin(qr) e^{-3Zr/2a_0} - \frac{Z}{a_0} \int_0^\infty r^2 \sin(qr) e^{-3Zr/2a_0} dr \right) \quad (89)$$

$$= \frac{Z^3}{\sqrt{2}a_0^3q} \left(2 \left[\frac{48a^3qZ}{(4a^2q^2 + 9Z^2)^2} \right] - \frac{Z}{a_0} \left[-\frac{32a^4q(4a^2q^2 - 27Z^2)}{(4a^2q^2 + 9Z^2)^3} \right] \right) \quad (90)$$

$$= \frac{2Z^4}{\sqrt{2}} \left(\frac{48}{(4a^2q^2 + 9Z^2)^2} + \frac{16(4a^2q^2 - 27Z^2)}{(4a^2q^2 + 9Z^2)^3} \right) \quad (91)$$

$$= \sqrt{2}Z^4 \left(\frac{48(4a^2q^2 + 9Z^2) + 16(4a^2q^2 - 27Z^2)}{(4a^2q^2 + 9Z^2)^3} \right) \quad (92)$$

$$= \sqrt{2}Z^4 \left(\frac{256a_0^2q^2}{(4a^2q^2 + 9Z^2)^3} \right) \quad (93)$$

$$(94)$$

Using these results, we have

$$\Delta_{\text{d}}(2, 0, 0) = \int \frac{d^3q}{(2\pi)^3} \left(\frac{Z^4}{\left[Z^2 + \left(\frac{a_0q}{2} \right)^2 \right]^2} \right) \frac{4\pi e^2}{q^2} \left(\frac{Z^4(a_0^2q^2 - Z^2)(2a_0^2q^2 - Z^2)}{(a_0^2q^2 + Z^2)^4} \right) \quad (95)$$

$$\Delta_{\text{ex}}(2, 0, 0) = \int \frac{d^3q}{(2\pi)^3} \left| \sqrt{2}Z^4 \left(\frac{256a_0^2q^2}{(4a^2q^2 + 9Z^2)^3} \right) \right|^2 \frac{4\pi e^2}{q^2}, \quad (96)$$

with first order energy shifts $\Delta E^{(1)}$ given by

$$\Delta E^{(1)} = \Delta_{\text{d}}(2, 0, 0) - P_{12}(S)\Delta_{\text{ex}}(2, 0, 0), \quad (97)$$

where $P_{12}(S = 0)$ is -1 for the spin singlet (2^1S) state and $P_{12}(S = 1)$ is $+1$ for the spin triplet (2^3S). Note that the direct and exchange integrals are over three components of q but, there is no angular dependence, so when we switch to spherical coordinates, we can immediately integrate over the polar and azimuthal angles, yielding a factor of 4π :

$$\Delta_{\text{d}}(2, 0, 0) = Z^8 \frac{(4\pi)^2}{(2\pi)^3} \int_0^\infty (q^2 dq) \frac{e^2}{q^2} \left(\frac{(a_0^2q^2 - Z^2)(2a_0^2q^2 - Z^2)}{(a_0^2q^2 + Z^2)^4 \left(Z^2 + \left(\frac{a_0q}{2} \right)^2 \right)^2} \right) \quad (98)$$

$$\Delta_{\text{ex}}(2, 0, 0) = Z^8 \frac{(4\pi)^2}{(2\pi)^3} \int_0^\infty (q^2 dq) \frac{(2e^2q^2)2^{16}a_0^4}{(4a^2q^2 + 9Z^2)^6}, \quad (99)$$

and note that $(4\pi)^2/(2\pi)^3 = 2/\pi$. The integrals simplify to

$$\frac{a}{e^2} \Delta_{\text{d}}(2, 0, 0) = Z^8 \frac{2a_0}{\pi} \int_0^\infty \frac{(a_0^2q^2 - Z^2)(2a_0^2q^2 - Z^2)}{(a_0^2q^2 + Z^2)^4 \left(Z^2 + \left(\frac{a_0q}{2} \right)^2 \right)^2} dq \quad (100)$$

$$\frac{a}{e^2} \Delta_{\text{ex}}(2, 0, 0) = Z^8 \frac{2^{18}a_0}{\pi} \int_0^\infty \frac{a_0^4q^4}{(4a^2q^2 + 9Z^2)^6} dq, \quad (101)$$

and if we define $x = qa_0$, the integrals become

$$\frac{a}{e^2} \Delta_d(2, 0, 0) = Z^8 \frac{2a_0}{\pi} \int_0^\infty \frac{(x^2 - Z^2)(2x^2 - Z^2)}{(x^2 + Z^2)^4 (Z^2 + \frac{1}{4}x^2)^2} dx \quad (102)$$

$$= \frac{2Z^8}{\pi} \int_0^\infty \frac{(x^2 - Z^2)(2x^2 - Z^2)}{(x^2 + Z^2)^4 (Z^2 + \frac{1}{4}x^2)^2} dx \quad (103)$$

$$\frac{a}{e^2} \Delta_{\text{ex}}(2, 0, 0) = Z^8 \frac{2^{18}a_0}{\pi} \int_0^\infty \frac{x^4}{(4x^2 + 9Z^2)^6} \frac{dx}{a_0} = \frac{2^{18}Z^8}{\pi} \int_0^\infty \frac{x^4}{(4x^2 + 9Z^2)^6} dx . \quad (104)$$

Letting MATHEMATICA handle the integrals:

$$\int_0^\infty \frac{(x^2 - Z^2)(2x^2 - Z^2)}{(x^2 + Z^2)^4 (Z^2 + \frac{1}{4}x^2)^2} dx = \frac{17\pi}{162Z^7} \quad (105)$$

$$\int_0^\infty \frac{x^4}{(4x^2 + 9Z^2)^6} dx = \frac{\pi}{11943936Z^7} , \quad (106)$$

yields the result

$$\frac{2a}{e^2} \Delta_d(2, 0, 0) = \frac{2^2 Z^8}{\pi} \frac{17\pi}{162Z^7} = \frac{34}{81} Z \quad (107)$$

$$\frac{2a}{e^2} \Delta_{\text{ex}}(2, 0, 0) = \frac{2^{19} Z^8}{\pi} \frac{\pi}{11943936Z^7} = \frac{2^{19}}{11943936} Z = \frac{32}{729} Z . \quad (108)$$

Using the definition of the Rydberg $R_H = e^2/2a_0$, we have

$$\Delta_d(2, 0, 0) = \frac{34}{81} Z R_H \quad (109)$$

$$\Delta_{\text{ex}}(2, 0, 0) = \frac{32}{729} Z R_H , \quad (110)$$

and for Helium, we have

$$\Delta_d(2, 0, 0) = \frac{68}{81} R_H = 11.4173 \text{ eV} \quad (111)$$

$$\Delta_{\text{ex}}(2, 0, 0) = \frac{64}{729} R_H = 1.194 \text{ eV} . \quad (112)$$

The energy of the [1s 2s] states are

$$E(2s; S) = \left(-5 + \frac{68}{81} - P_{12}(S) \frac{64}{729} \right) R_H , \quad (113)$$

so for the ‘‘ortho’’ (spin-triplet, 2^3S) state, we have

$$E(2s; 1) = \left(-5 + \frac{68}{81} - \frac{64}{729} \right) R_H = \left(-5 + \frac{548}{729} \right) R_H = -57.7767 \text{ eV} , \quad (114)$$

and for the ‘‘para’’ (spin-singlet, 2^1S) state, we have

$$E(2s; 0) = \left(-5 + \frac{676}{729} \right) R_H = -55.3888 \text{ eV} , \quad (115)$$

and we see the symmetric spin states have lower energies (are more tightly bound to the nucleus). The ground state of neutral helium, ignoring the repulsion of the electrons is $E_{[1s\ 1s]} = -8R_H = -108.8$ eV, and the unperturbed first excited state is $E_{[1s\ 2s]} = -5R_H = -68$ eV. Including the Coulomb repulsion, the energies of the “ortho” and “para” states, are given above. NIST gives the values of the $[1s\ 2s]$ states of helium to be

$$E_{2^1s}^{\text{NIST}} = 166277.4403 \text{ cm}^{-1} = 20.6161 \text{ eV} \quad (116)$$

$$E_{2^3s}^{\text{NIST}} = 159855.9745 \text{ cm}^{-1} = 19.8199 \text{ eV}. \quad (117)$$

using the conversion factor $1 \text{ cm}^{-1} = 0.000123986 \text{ eV}$. These are measured relative to the ground state, which is $-8R_H = -108.8$ eV, (note this is the estimate for neglecting the electrons’ mutual repulsion, the correct ground state energy is⁴ -78.98 eV) so the energy of these states relative to the continuum is

$$\text{para} : E_{2^1s}^{\text{NIST}} = 20.6161 - 78.98 \text{ eV} = -59.3639 \text{ eV} \quad (118)$$

$$\text{ortho} : E_{2^3s}^{\text{NIST}} = 19.8199 - 78.98 \text{ eV} = -60.1601 \text{ eV}, \quad (119)$$

so the first-order perturbation theory results have errors of 6.69% and 3.96% for the $[1s\ 2s]$ para and ortho states, respectively.

⁴Richard Fitzpatrick, “Helium Atom”, <http://farside.ph.utexas.edu/teaching/qmech/Quantum/node128.html>.