

Homework H28 Solution

1. Problem 7.2 in the book.

Solution: For the first excited state, the symmetric and anti-symmetric spatial wavefunctions are given respectively by,

$$\psi_s = \frac{1}{\sqrt{2}} [\phi_{1s}(1)\phi_{2s}(2) + \phi_{1s}(2)\phi_{2s}(1)]$$

and

$$\psi_a = \frac{1}{\sqrt{2}} [\phi_{1s}(1)\phi_{2s}(2) - \phi_{1s}(2)\phi_{2s}(1)]$$

For 2 electrons being in two different spatial orbitals, there are 4 allowed spin functions, of which 3 are symmetric,

$$\begin{aligned} & \alpha(1)\alpha(1) \\ & \beta(1)\beta(2) \\ & \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) + \alpha(2)\beta(1)] \end{aligned}$$

and 1 is anti-symmetric,

$$\frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \alpha(2)\beta(1)]$$

To keep the overall wavefunction anti-symmetric, the anti-symmetric spatial function can combine with either of the 3 symmetric spin functions, giving rise to a triply degenerate (triplet) state; whereas, the symmetric spatial function can combine with the only anti-symmetric spin function, thus forming a singlet state.

So the singlet state is given by ,

$$\frac{1}{2} [\phi_{1s}(1)\phi_{2s}(2) + \phi_{1s}(2)\phi_{2s}(1)] [\alpha(1)\beta(2) - \alpha(2)\beta(1)]$$

This is a singlet state because the electrons can have only opposite spin, thus giving $2s + 1 = 2 \left(\frac{1}{2} - \frac{1}{2} \right) + 1 = 1$ as the degeneracy of the state.

2. **Turn in** Time, for once, to calculate one of those horrible matrix elements Gruebele mentions in lecture explicitly. Consider the He ground state $|\psi\rangle = |\phi\rangle_1 |\phi\rangle_2 \frac{1}{\sqrt{2}} [|\alpha_1\rangle |\beta_2\rangle - |\beta_1\rangle |\alpha_2\rangle]$, evaluate the one-electron kinetic energy integral of the total energy expression.

a. First show stepwise the missing steps that prove lines 2 and 3 (leaving out the constant electron-electron repulsion energy):

$$\begin{aligned} \langle E \rangle &= \langle \psi | \hat{H} | \psi \rangle \\ &= 2 \langle \phi_1 | \hat{h}_1 | \phi_1 \rangle + \langle \phi_1 | \langle \phi_2 | \frac{1}{r_{12}} | \phi_1 \rangle | \phi_2 \rangle \end{aligned}$$

$$2\langle\phi_1|\hat{h}_1|\phi_1\rangle = -\langle\phi_1|\nabla^2|\phi_1\rangle - 2\left\langle\phi_1\left|\frac{Z}{r_1}\right|\phi_1\right\rangle$$

Solution:

$$\begin{aligned}\langle E \rangle &= \left\langle\phi_1\left|\left\langle\phi_2\left|\left\{\hat{h}_1 + \hat{h}_2 + \frac{1}{r_{12}}\right\}|\phi_1\right\rangle|\phi_2\right\rangle \cdot \frac{1}{2}[(\langle\alpha_1|\langle\beta_2| - \langle\beta_1|\langle\alpha_2|) \cdot (|\alpha_1\rangle|\beta_2\rangle - |\beta_1\rangle|\alpha_2\rangle)]\right. \\ &\quad \left. + \frac{1}{r_{12}}\right\}|\phi_1\rangle|\phi_2\rangle \cdot \frac{1}{2}[(\langle\alpha_1|\langle\beta_2| - \langle\beta_1|\langle\alpha_2|) \cdot (|\alpha_1\rangle|\beta_2\rangle - |\beta_1\rangle|\alpha_2\rangle)]\end{aligned}$$

This separation of spatial and spin parts are possible because the Hamiltonian operator does not operate on the spin functions. Thus,

$$\begin{aligned}\langle E \rangle &= \left\langle\phi_1\left|\left\langle\phi_2\left|\left\{\hat{h}_1 + \hat{h}_2 + \frac{1}{r_{12}}\right\}|\phi_1\right\rangle|\phi_2\right\rangle \cdot \frac{1}{2}[1 - 0 - 0 + 1]\right. \\ &= \langle\phi_1|\hat{h}_1|\phi_1\rangle\langle\phi_2|\phi_2\rangle + \langle\phi_2|\hat{h}_2|\phi_2\rangle\langle\phi_1|\phi_1\rangle + \left\langle\phi_1\left|\left\langle\phi_2\left|\frac{1}{r_{12}}\right|\phi_1\right\rangle|\phi_2\right\rangle\end{aligned}$$

This comes from the fact that the one-electron Hamiltonian for one atom does not act on the other. Further, each of these two terms are equal, since the 2 atoms are of course identical. Thus,

$$\langle E \rangle = 2\langle\phi_1|\hat{h}_1|\phi_1\rangle + \left\langle\phi_1\left|\left\langle\phi_2\left|\frac{1}{r_{12}}\right|\phi_1\right\rangle|\phi_2\right\rangle$$

Now, $\hat{h}_1 = -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{4\pi\epsilon r_1} = -\frac{1}{2}\nabla^2 - \frac{Z}{r_1}$ in atomic units. Therefore,

$$2\langle\phi_1|\hat{h}_1|\phi_1\rangle = -\langle\phi_1|\nabla^2|\phi_1\rangle - 2\left\langle\phi_1\left|\frac{1}{r_1}\right|\phi_1\right\rangle$$

- b. If the 1s wavefunction is $\phi_1 = C \exp(-Z_{eff}r_1)$ for electron #1, why is it good enough to use for ∇^2 just the $\frac{1}{r_1^2} \frac{\partial}{\partial r_1} r_1^2 \frac{\partial}{\partial r_1}$ radial part?

Solution: The 1s wavefunction is spherically symmetric, that is it has no angular dependence. Thus the angular part of the Laplacian operator does not operate on the wavefunction. Hence it is good enough to write as,

$$\nabla_1^2 = \frac{1}{r_1^2} \frac{\partial}{\partial r_1} r_1^2 \frac{\partial}{\partial r_1}$$

- c. Normalize the wavefunction and evaluate the integral. [Hint: When you integrate over spherical co-ordinates, you get a factor of $4\pi \int_0^\infty r^2 dr$, which should be familiar by now.]

Solution: To normalize, we have,

$$C^2 \int_0^{\infty} 4\pi r_1^2 dr_1 e^{-2Z_{eff}r_1} = 1$$

$$C^2 \frac{\pi}{Z_{eff}^3} = 1$$

or,

$$C = \sqrt{\frac{Z_{eff}^3}{\pi}}$$

Therefore,

$$-\langle \phi_1 | \nabla^2 | \phi_1 \rangle = -\frac{Z_{eff}^3}{\pi} 4\pi \int_0^{\infty} r_1^2 dr_1 e^{-Z_{eff}r_1} \left\{ \frac{1}{r_1^2} \frac{\partial}{\partial r_1} r_1^2 \frac{\partial}{\partial r_1} \right\} e^{-Z_{eff}r_1}$$

$$= -4 Z_{eff}^3 \int_0^{\infty} r_1^2 dr_1 e^{-Z_{eff}r_1} \left[Z_{eff}^2 - \frac{2Z_{eff}}{r_1} \right] e^{-Z_{eff}r_1}$$

$$= -4 Z_{eff}^5 \int_0^{\infty} r_1^2 dr_1 e^{-2Z_{eff}r_1} + 8 Z_{eff}^4 \int_0^{\infty} r_1 dr_1 e^{-2Z_{eff}r_1}$$

$= -Z_{eff}^2 + 2Z_{eff}^2 = Z_{eff}^2$ (use an online integrator for $\int dx x \exp(-ax)$ and the like). Similarly one could calculate the integrals over the $-1/r_1$ electron-nuclear attraction and over the $+1/r_{12}$ electron repulsion and get the whole matrix element for He. We then took the derivative with respect to Z_{eff} in class to find the optimal variation of the basis function $e^{-Z_{eff}r_1}$ that gives the lowest energy (and thus closest to the actual energy).

3. Gruebele claimed in class that just truncating (leaving out) high energy basis states from a Hamiltonian matrix when diagonalizing on the computer can give accurate results for the low energy eigenfunctions. Test this proposition by numerically diagonalizing the matrices

$$\begin{pmatrix} 1 & 1.5 & 1.5 \\ 1.5 & 2 & 1.5 \\ 1.5 & 1.5 & 100 \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} 1 & 1.5 \\ 1.5 & 2 \end{pmatrix}$$

Think of the first as the “full problem,” and the second as the truncated problem. Are the two lowest eigenvalues of the first matrix very different from the eigenvalues of the second matrix? Would this truncation be accurate to 1%?

Solution: Using the app to numerically diagonalize the first matrix results in the three eigenvalues

$$E_1 = -0.082309, E_2 = 3.035938, E_3 = 100.046371$$

Again using the app, the eigenvalues of the second matrix are

$$E_1 = -0.081139, E_2 = 3.081139$$

Both of the truncated two lowest eigenvalues differ from their counterparts in the “full problem” by $\sim 1.5\%$, so the truncation would be accurate to between $\sim 1\%$ and 2% .

4. Calculate the two lowest eigenvalues of the matrix

$$\begin{pmatrix} 1 & 0.1 & 0 & -0.1 \\ 0.1 & 3 & 0.2 & 0 \\ 0 & 0.2 & 7 & 1 \\ -0.1 & 0 & 1 & 19 \end{pmatrix}$$

and compare it with the eigenvalues of $\begin{pmatrix} 1 & 0.1 \\ 0.1 & 3 \end{pmatrix}$, to prove that the Hylleraas – Undheim theorem holds for the truncated matrix in the upper lefthand corner.

Solution: Using the app given in a previous homework to calculate eigenvalues, we see that the two lowest eigenvalues of the 4 X 4 matrix are 0.9944 and 2.9948.

Diagonalizing the truncated 2 by 2 matrix gives us eigenvalues 0.9950 and 3.0049. This shows that the actual eigenvalues of the original matrix are lower than the eigenvalues of the truncated matrix. Thus, the approximate eigenvalues (obtained by truncating the matrix) are the upper limits of the real eigenvalues. This shows the validity of the Hylleraas – Undheim theorem for this special case.