

Nov. 12, 2007

Chem. 1410

Problem Set 8, due Nov. 19, 2007

Do the following problems; these are *not* to be handed in for grading; solutions will be distributed via .pdf.

Engel Chapter 10: P10.3, P10.6, P10.9, P10.11, P10.14, P10.18

The following two problems are to be handing in for grading:

1) Slater Determinants and the 1s2s Electronic State Configuration of the He atom. Consider the 1s2s electronic configuration of the helium atom, viz., one electron is in a 1s-type orbital and the other is in a 2s-type orbital. One possible (unnormalized) Slater determinant for this configuration is:

$$\begin{vmatrix} 1s(1)\alpha(1) & 2s(1)\beta(1) \\ 1s(2)\alpha(2) & 2s(2)\beta(2) \end{vmatrix}$$

where 1s(1) is a one-electron hydrogen 1s orbital corresponding to coordinate \vec{r}_1 , $\alpha(1)$ means that electron 1 is in a spin up state, etc.

a) Find 3 other possible Slater determinants of the same type.

b) Show that the 4 Slater determinants constructed in part *a* are equivalent to the following 4 spin-orbitals:

i) $[1s(1)2s(2) + 1s(2)2s(1)][\alpha(1)\beta(2) - \alpha(2)\beta(1)]$

ii) $[1s(1)2s(2) - 1s(2)2s(1)]\alpha(1)\alpha(2)$

iii) $[1s(1)2s(2) - 1s(2)2s(1)]\beta(1)\beta(2)$

iv) $[1s(1)2s(2) - 1s(2)2s(1)][\alpha(1)\beta(2) + \alpha(2)\beta(1)]$

[Note: you may need to take linear combinations of the Slater determinants found in part *a* to generate some of the above terms.]

Comments: Note that each member of *i-iv* is antisymmetric to the exchange of the electron labels, as it must be according to the Pauli Exclusion Principle. Term *i* differs from terms *ii-iv* in that its spatial factor

is symmetric to exchange of electron labels, while its spin factor is antisymmetric to exchange of electron labels: in terms $ii-iv$ the situation is reversed. Term i is called a “singlet” state, while terms $ii-iv$ are known as “triplet” states. They have different properties, including the spatial distribution of the electrons and the state energy.

2) **Variational Principle Treatment of the He Atom Ground State.** Recall that the Hamiltonian for He (nuclear charge $Z=2$) is

$$\hat{H} = \frac{-\hbar^2}{2m_e}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{2\pi\epsilon_0} \left(\frac{1}{r_1} + \frac{1}{r_2} \right) + \frac{e^2}{4\pi\epsilon_0 r_{12}} ,$$

where ∇_1^2 is the Laplacian for electron 1, r_1 is the distance of electron 1 from the nucleus, and r_{12} is the distance between the two electrons. In this problem, we’ll consider a normalized variational trial function of the form $\psi_T(\vec{r}_1, \vec{r}_2) = \phi_1(r_1; \xi)\phi_{1s}(r_2; \xi)$, where $\phi_{1s}(r; \xi)$ is a normalized hydrogenic orbital corresponding to nuclear charge ξ . Explicitly,

$$\phi_{1s}(r; \xi) = \pi^{-1/2} (\xi / a_0)^{3/2} \exp(-\xi r / a_0) ,$$

where a_0 is the H-atom Bohr radius. We will regard ξ as a variational parameter and minimize $\langle \psi_T | \hat{H} | \psi_T \rangle$ with respect to ξ in order to find the best approximation to the He ground state that can be obtained with a trial function of the adopted form.

(a) Show that the Hamiltonian can be rewritten as

$$\hat{H} = \hat{h}_1(\xi) + \hat{h}_2(\xi) + (\xi - 2) \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_1} + \frac{1}{r_2} \right) + \frac{e^2}{4\pi\epsilon_0 r_{12}} ,$$

where $\hat{h}_1(\xi)$ is the hydrogenic Hamiltonian

$$\hat{h}_1(\xi) = \frac{-\hbar^2}{2m_e} \nabla_1^2 - \frac{\xi e^2}{4\pi\epsilon_0} \frac{1}{r_1} ,$$

and likewise for $\hat{h}_2(\xi)$.

(b) Show that

$$\langle \psi_T | \hat{h}_1(\xi) + \hat{h}_2(\xi) | \psi_T \rangle = -\xi^2 e^2 / 4\pi\epsilon_0 a_0 ,$$

[Hint: $\phi_{1s}(r_1; \xi)$ is an eigenfunction of $\hat{h}_1(\xi)$.]

(c) By direct integration it is straightforward to show that $\langle \psi_T | r_1^{-1} | \psi_T \rangle = \xi / a_0$. Moreover, it is possible to evaluate $\langle \psi_T | r_{12}^{-1} | \psi_T \rangle = \frac{5\xi}{8a_0}$. Putting together these facts and the results of parts (a) and (b), show that

$$E(\xi) \equiv \langle \psi_T | \hat{H} | \psi_T \rangle = \frac{e^2}{8\pi\epsilon_0 a_0} \{-2\xi^2 + 4(\xi - 2)\xi + 5\xi/4\}$$

(d) Find the value of ξ for which $E(\xi)$ is a minimum. This determines the variationally optimal approximation to both the ground state eigenfunction and energy level for He.

(e) Is $\xi < 2$ or $\xi > 2$? Interpret your result.

(f) What is the approximate ground state energy eigenvalue predicted by this calculation? Give your answer in eV. [Remember: $\frac{e^2}{8\pi\epsilon_0 a_0} = 13.6 \text{ eV}$.] Compare your approximate solution to the known exact value of -79.0eV. How good is the agreement?