

量子化学作业 第八章 (2017-2018 学期)

1. Show that the expression for α in a trial function $e^{-\alpha r^2}$ for a hydrogen atom is given by $\alpha = 8/9a_0^2$, where a_0 is the Bohr radius.

2. If you were to use a trial function of the form $\phi(x) = (1 + c\alpha x^2)e^{-\alpha x^2/2}$, where $\alpha = (k\mu/\hbar^2)^{1/2}$ and c is a variational parameter, to calculate the ground-state energy of a harmonic oscillator, what do you think the value of c will come out to be? Why?

3. Consider a three-dimensional, spherically symmetric, isotropic harmonic oscillator with $V(r) = kr^2/2$. Using a trial function $e^{-\alpha r^2}$ with α as a variational parameter, calculate the ground-state energy. Do the same using $e^{-\alpha r}$. The Hamiltonian operator is

$$\hat{H} = -\frac{\hbar^2}{2\mu r^2} \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) + \frac{1}{2} kr^2$$

Compare these results with the exact ground-state energy, $E = 3/2\hbar\omega$. Why is one of them so much better than the other?

4. Use a trial function of the form $e^{-\alpha x^2/2}$ to calculate the ground-state energy of a quartic oscillator, whose potential is $V(x) = cx^4$.

5. Consider a particle of mass m in the potential energy field described by

$$V(x) = \begin{cases} V_0 & x < -a \\ 0 & -a < x < a \\ V_0 & x > a \end{cases}$$

This problem describes a particle in a finite well. If $V_0 \rightarrow \infty$, then we have a particle in a box. Using $\phi(x) = l^2 - x^2$ for $-l < x < l$ and $\phi(x) = 0$ otherwise as a trial function with l as a variational parameter, calculate the ground-state energy of this system for two conditions with $2mV_0a^2 / \hbar^2 = 4$ and 12 respectively.

(As a reference, the exact ground-state energies are $0.530\hbar^2 / ma^2$ and $0.736\hbar^2 / ma^2$, respectively)

6. Repeat the calculation in the previous problem for a trial function $\phi(x) = \cos \lambda x$ for $-\pi/2\lambda < x < \pi/2\lambda$ and $\phi(x) = 0$ otherwise. Use λ as a variational parameter.

7. (a) In this problem, we will solve the Schrödinger equation for the ground-state wave function and energy of a particle confined to a sphere of radius a . The Schrödinger equation is given by

$$-\frac{\hbar^2}{2m} \frac{d}{dr} \left(r^2 \frac{d\psi}{dr} \right) = E\psi$$

Substitute $u = r\psi$ into this equation to get

$$\frac{d^2 u}{dr^2} + \frac{2mE}{\hbar^2} u = 0$$

The general solution to this equation is

$$u(r) = A \cos \alpha r + B \sin \alpha r$$

or

$$\psi(r) = \frac{A \cos \alpha r}{r} + \frac{B \sin \alpha r}{r}$$

where $\alpha = (2mE/\hbar^2)^{1/2}$. Which of these terms is finite at $r=0$? Now use the fact that $\phi(a)=0$ to prove that

$$\alpha a = \pi$$

for the ground state, or that the ground-state energy is

$$E = \frac{\pi^2 \hbar^2}{2ma^2}$$

Show that the normalized ground-state wave function is

$$\psi(r) = (2\pi a)^{-1/2} \frac{\sin \pi r / a}{r}$$

(b) Use $\phi(r) = a - r$ as an approximate wave function to calculate an approximate ground-state energy of this system. Compare your result to the exact energy obtained from the previous problem to show the variational principle.

8. What does the secular determinant in Equation 8.39 look like if we expand ϕ in Equation 8.24 in an orthonormal set of functions? (Page 388 and Page 393 of the textbook)

9. This problem shows that terms in a trial function that correspond to progressively higher energies contribute progressively less to the ground-state energy. For algebraic simplicity, assume that the Hamiltonian operator can be written in the form

$$\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)}$$

and choose a trial function

$$\phi = c_1\psi_1 + c_2\psi_2$$

where

$$\hat{H}^{(0)}\psi_j = E_j^{(0)}\psi_j \quad j = 1, 2$$

show that the secular equation associated with the trial function is

$$\begin{vmatrix} H_{11} - E & H_{12} \\ H_{12} & H_{22} - E \end{vmatrix} = \begin{vmatrix} E_1^{(0)} + E_1^{(1)} - E & H_{12} \\ H_{12} & E_2^{(0)} + E_2^{(1)} - E \end{vmatrix} = 0 \quad (1)$$

where

$$E_j^{(1)} = \int \psi_j^* \hat{H}^{(1)} \psi_j d\tau \quad \text{and} \quad H_{12} = \int \psi_1^* \hat{H}^{(1)} \psi_2 d\tau$$

Solve equation 1 for E to obtain

$$E = \frac{E_1^{(0)} + E_1^{(1)} + E_2^{(0)} + E_2^{(1)}}{2} \pm \frac{1}{2} \{ [E_1^{(0)} + E_1^{(1)} - E_2^{(0)} - E_2^{(1)}]^2 + 4H_{12}^2 \}^{1/2} \quad (2)$$

If we arbitrarily assume that $E_1^{(0)} + E_1^{(1)} < E_2^{(0)} + E_2^{(1)}$, then we take the positive sign in equation 2 and write

$$E = \frac{E_1^{(0)} + E_1^{(1)} + E_2^{(0)} + E_2^{(1)}}{2} + \frac{E_1^{(0)} + E_1^{(1)} - E_2^{(0)} - E_2^{(1)}}{2} \times \left\{ 1 + \frac{4H_{12}^2}{[E_1^{(0)} + E_1^{(1)} - E_2^{(0)} - E_2^{(1)}]^2} \right\}^{1/2}$$

Use the expansion $(1+x)^{1/2} = 1+x/2+\dots$ to get

$$E = E_1^{(0)} + E_1^{(1)} + \frac{H_{12}^2}{E_1^{(0)} + E_1^{(1)} - E_2^{(0)} - E_2^{(1)}} + \dots \quad (3)$$

Note that if $E_1^{(0)} + E_1^{(1)}$ and $E_2^{(0)} + E_2^{(1)}$ are widely separated, the term involving H_{12}^2 in equation 3 is small. Therefore, the energy is simply that calculated using ψ_1 alone; the ψ_2 part of the trial function contributes little to the overall energy. The general result is that terms in a trial function that correspond to higher and higher energies contribute less and less to the total ground-state energy.

10. Verify the expansion in Equation 8.57 (Page 400 of the textbook)

11. Calculate the first-order correction to the first excited state of an anharmonic oscillator whose potential is given in Example 8-5. (Page 402 of the textbook)

12. Use first-order perturbation theory to calculate the first-order correction to the ground state energy of a quartic oscillator whose potential energy is

$$V(x) = cx^4$$

In this case, use a harmonic oscillator as the unperturbed system. What is the perturbing potential?

13. True or false? The second-order correction energy $E_0^{(2)}$ to the ground-state energy is never positive. Show your reason.

14. In Example 5-2, we introduced the Morse potential

$$V(x) = D(1 - e^{-\beta x})^2$$

as a description of the internuclear potential energy of a diatomic molecule. First expand the Morse potential in a power series about x . (Hint: Use the expansion $e^x = 1 + x + x^2/2 + x^3/6 + \dots$) What is the Hamiltonian operator for the Morse potential? Show that the Hamiltonian operator can be written in the form

$$\hat{H} = -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + ax^2 + bx^3 + cx^4 + \dots$$

How are the constants a , b , and c related to the constants D and β ? What part of the Hamiltonian operator would you associate with $\hat{H}^{(0)}$, and what are the functions $\psi_n^{(0)}$ and energies $E_n^{(0)}$? Use perturbation theory to evaluate the first-order corrections to the energy of the first three states that arise from the cubic and quartic terms.

15. In applying first-order perturbation theory to a helium atom, we must evaluate the integral

$$E^{(1)} = \frac{e^2}{4\pi\epsilon_0} \iint d\mathbf{r}_1 d\mathbf{r}_2 \psi_{1s}^*(\mathbf{r}_1) \psi_{1s}^*(\mathbf{r}_2) \frac{1}{r_{12}} \psi_{1s}(\mathbf{r}_1) \psi_{1s}(\mathbf{r}_2)$$

where

$$\psi_{1s}(\mathbf{r}_j) = \left(\frac{Z^3}{a_0^3 \pi} \right)^{1/2} e^{-Zr_j/a_0}$$

and $Z = 2$ for a helium atom. This same integral occurs in a variational treatment of a helium atom, where in that case the value of Z is left arbitrary. This problem proves that

$$E^{(1)} = \frac{5Z}{8} \left(\frac{m_e e^4}{16\pi^2 \epsilon_0^2 \hbar^2} \right)$$

Let \mathbf{r}_1 and \mathbf{r}_2 be the radius vectors of electrons 1 and 2, respectively, and let θ be the angle between these two vectors. Now this is generally not the θ of spherical coordinates, but if we choose one of the radius vectors, say \mathbf{r}_1 , to be the z axis, then the two θ 's are the same. Using the law of cosines,

$$r_{12} = (r_1^2 + r_2^2 - 2r_1 r_2 \cos \theta)^{1/2}$$

show that $E^{(1)}$ becomes

$$E^{(1)} = \frac{e^2}{4\pi\epsilon_0} \frac{Z^6}{a_0^6 \pi^2} \int_0^\infty dr_1 e^{-Zr_1/a_0} r_1^2 \int_0^\infty dr_2 e^{-Zr_2/a_0} r_2^2 \\ \times \int_0^{2\pi} d\phi \int_0^\pi \frac{d\theta \sin \theta}{(r_1^2 + r_2^2 - 2r_1 r_2 \cos \theta)^{1/2}}$$

Letting $x = \cos \theta$, show that the integrand over θ is

$$\int_0^\pi \frac{d\theta \sin \theta}{(r_1^2 + r_2^2 - 2r_1 r_2 \cos \theta)^{1/2}} = \int_{-1}^1 \frac{dx}{(r_1^2 + r_2^2 - 2r_1 r_2 \cos \theta)^{1/2}} = \begin{cases} \frac{2}{r_1} & r_1 > r_2 \\ \frac{2}{r_2} & r_1 < r_2 \end{cases}$$

Substituting this result into $E^{(1)}$, show that

$$\begin{aligned}
E^{(1)} &= \frac{e^2}{4\pi\epsilon_0} \frac{16Z^6}{a_0^6} \int_0^\infty dr_1 e^{-2Zr_1/a_0} r_1^2 \left(\frac{1}{r_1} \int_0^{r_1} dr_2 e^{-2Zr_2/a_0} r_2^2 + \int_{r_1}^\infty dr_2 e^{-2Zr_2/a_0} r_2 \right) \\
&= \frac{e^2}{4\pi\epsilon_0} \frac{4Z^3}{a_0^3} \int_0^\infty dr_1 e^{-2Zr_1/a_0} r_1^2 \left[\frac{1}{r_1} - e^{-2Zr_1/a_0} \left(\frac{Z}{a_0} + \frac{1}{r_1} \right) \right] \\
&= \frac{5}{8} Z \left(\frac{e^2}{4\pi\epsilon_0 a_0} \right) = \frac{5}{8} Z \left(\frac{m_e e^4}{16\pi^2 \epsilon_0^2 \hbar^2} \right)
\end{aligned}$$

Show that the energy through first order is

$$\begin{aligned}
E^{(0)} + E^{(1)} &= \left(-Z^2 + \frac{5}{8} Z \right) \left(\frac{m_e e^4}{16\pi^2 \epsilon_0^2 \hbar^2} \right) = -\frac{11}{4} \left(\frac{m_e e^4}{16\pi^2 \epsilon_0^2 \hbar^2} \right) \\
&= -2.75 \left(\frac{m_e e^4}{16\pi^2 \epsilon_0^2 \hbar^2} \right)
\end{aligned}$$

Compared with the exact result $E_{\text{exact}} = -2.9037(m_e e^4 / 16\pi^2 \epsilon_0^2 \hbar^2)$, what is the error in kcal/mol? (Hint: refer to the definition of atomic units, instead of numerical calculation directly.)

Mathematics:

1. Show that $(\mathbf{AB})^\dagger = \mathbf{B}^\dagger \mathbf{A}^\dagger$

2. Show that $\text{Tr} \mathbf{AB} = \text{Tr} \mathbf{BA}$.