

## Exercise 09

HAND IN YOUR SOLUTIONS BEFORE NEXT FRIDAY AT 8.00 AM OR SEND AN EMAIL  
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## 1 Perturbation theory applied to diatomic molecule (15 Points)

We introduce the Morse potential as a description of the intramolecular potential energy of a diatomic molecule:

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

with  $x = r - r_e$ , where  $r$  is the distance between two atoms and  $r_e$  is the equilibrium distance. The constants  $D$  and  $\beta$  are different for each molecule (for  $\text{H}_2$ :  $D = 7.61 \times 10^{-19}$  J and  $\beta = 0.0193$  pm<sup>-1</sup>).

First expand the Morse potential in a power series about  $x$  (hint: Use the expansion  $e^x = 1 + x + \frac{x^2}{2} + \frac{x^3}{6} + \dots$ ).

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  $a$ ,  $b$ ,  $c$ , related to the constants  $D$  and  $\beta$ ? 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 the perturbation theory to evaluate the first-order corrections to the energy of the first three states that arise from the cubic and quartic terms. Using these results, how different are the first two energy levels of  $\text{H}_2$  if its intramolecular potential is described by a harmonic oscillator potential or the quartic expansion of the Morse potential?

## 2 Perturbation theory applied to Helium atom (15 Points)

The Hamiltonian operator of the helium atom is

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + \hat{H}_{12} = -\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{2e^2}{4\pi\epsilon_0 r_1} - \frac{\hbar^2}{2m_e} \nabla_2^2 - \frac{2e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}}$$

where the terms in the above expression represent the kinetic energy of the first electron, the electrostatic attraction between the nucleus and the first electron; the kinetic energy of the second electron, the electrostatic attraction between the nucleus and the second electron; and the electrostatic repulsion between the two electrons, respectively. If we neglect the last term, the Hamiltonian just becomes the sum of separate Hamiltonians for each electron and we would expect the wavefunction to be separable:

$$\psi^{(0)}(\mathbf{r}_1, \mathbf{r}_2) = \psi(\mathbf{r}_1)\psi(\mathbf{r}_2)$$

and the Hamiltonian would have eigenvalues

$$E = E_1 + E_2$$

If we consider the ground state, both electrons are in their lowest energy states with wavefunctions:

$$\psi_{100}(\mathbf{r}_i) = \sqrt{\frac{Z^3}{a_0^3\pi}} e^{-Z\frac{r_i}{a_0}} \quad i = 1, 2$$

with  $Z = 2$ . The eigenvalues of Hydrogen-like atoms are:

$$E_{0,Z} = -\frac{m_e e^4 Z^2}{32\pi^2 \epsilon_0^2 \hbar^2}$$

Then for a Helium atom the ground state is:

$$E^{(0)} = E_{0,2} + E_{0,2} = 8E_{0,1} = -4E_h$$

where  $E_{0,1}$  is the ground state of the Hydrogen atom and  $E_h = -\frac{m_e e^4 Z^2}{16\pi^2 \epsilon_0^2 \hbar^2}$  is the Hartree energy. This result is very different from the experimentally determined value  $-2.9E_h$ .

This means that our initial approximation was wrong and that we cannot neglect the repulsive term between the electrons. On the other hand, the complete Hamiltonian of the Helium atom, including the repulsive term, is not separable anymore.

We can use the perturbation theory to improve our previous result, writing the ground state energy as sum of the unperturbed and repulsive term:

$$E = E^{(0)} + E^{(1)}$$

We already know the value of  $E^{(0)}$ , so we just need to compute the first order correction:

$$E^{(1)} = \langle \psi^{(0)}(\mathbf{r}_1, \mathbf{r}_2) | \hat{H}_{12} | \psi^{(0)}(\mathbf{r}_1, \mathbf{r}_2) \rangle = \frac{e^2}{4\pi\epsilon_0} \int_0^\infty \int_0^\infty d\mathbf{r}_1 d\mathbf{r}_2 \psi_{100}^*(\mathbf{r}_1) \psi_{100}^*(\mathbf{r}_2) \frac{1}{r_{12}} \psi_{100}(\mathbf{r}_1) \psi_{100}(\mathbf{r}_2) \quad (1)$$

where  $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ .

1. Simplify the integral (1), rewriting the term  $1/r_{12}$  as an expansion in terms of spherical harmonics

$$\frac{1}{r_{12}} = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} \frac{4\pi}{2l+1} \frac{r_{<}^l}{r_{>}^{l+1}} Y_l^m(\theta_1, \phi_1) Y_l^{m*}(\theta_2, \phi_2)$$

where  $r_{<}$  and  $r_{>}$  are, respectively, the smaller and larger values of  $r_1$  and  $r_2$ . For example if  $r_1 > r_2$ , then  $r_{<} = r_2$  and  $r_{>} = r_1$ . Setting correctly the integral, you should get the result

$$E^{(1)} = \frac{e^2}{4\pi\epsilon_0} \frac{16Z^6}{a_0^6} \int_0^\infty dr_1 r_1^2 e^{-2Zr_1/a_0} \int_0^\infty dr_2 \frac{e^{-2Zr_2/a_0}}{r_{>}}$$

2. Solve the integral and show that

$$E^{(1)} = \frac{5}{8} Z \left( \frac{e^2}{4\pi\epsilon_0 a_0} \right) = \frac{5}{8} Z \left( \frac{m_e e^4}{16\pi^2 \epsilon_0^2 \hbar^2} \right)$$

where we used  $a_0 = \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2}$ .

3. What is the ground state energy corrected with the perturbative term? Is the result improved?