22.1.4: iv. Problems 11-18

Q11

Consider an N_2 molecule, in the ground vibrational level of the ground electronic state, which is bombarded by 100 eV electrons. This leads to the ionization of the N_2 molecule to form N_2^+. In this problem we will attempt to calculate the vibrational distribution of the newly-formed N_2^+ ions, using a somewhat simplified approach.

a. Calculate (according to classical mechanics) the velocity (in cm/sec) of a 100 eV electron, ignoring any relativistic effects. Also calculate the amount of time required for a 100 eV electron to pass an N_2 molecule, which you may estimate as having a length of 2Å.

b. The radial Schrödinger equation for a diatomic molecule treating vibration as a harmonic oscillator can be written as:

$$-\frac{\hbar^2}{2\mu r^2}\left(\frac{\partial}{\partial r}\left(r^2\frac{\partial\Psi}{\partial r}\right)\right)+\frac{k}{2}(r-r_e)^2\Psi=E\Psi,$$

Substituting $\Psi(r)=\dfrac{F(r)}{r}$, this equation can be rewritten as:

$$-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2}F(r)+\frac{k}{2}(r-r_e)^2\Psi=E\Psi,$$

The vibrational Hamiltonian for the ground electronic state of the N2 molecule within this approximation is given by:

$$\mathbf{H}(N_2)=-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2}+\frac{k_{N_2}}{2}(r-r_{N_2}),$$

where r_{N_2} and k_{N_2} have been measured experimentally to be:

$$r_{N_2}=1.09796\text{Å};k_{N_2}=2.294x10^6\frac{\text{g}}{\text{sec}^2}.$$

The vibrational Hamiltonian for the N_2^+ ion , however, is given by :

$$\mathbf{H}(N_2)=-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2}+\frac{k_{N_2}^+}{2}\left(r-r_{N_2}^+\right)^2,$$

where $r_{N_2}^+$ and $k_{N_2}^+$ have been measured experimentally to be:

$$r_{N_2}^+=1.11642\text{Å};k_{N_2}^+=2.009x10^6\frac{\text{g}}{\text{sec}^2}$$

In both systems the reduced mass is $\mu=1.1624x10^{-23}g$. Use the above information to write out the ground state vibrational wavefunctions of the N_2 and N_2 + molecules, giving explicit values for any constants which appear in them. Note: For this problem use the "normal" expression for the ground state wavefunction of a harmonic oscillator. You need not solve the differential equation for this system.

c. During the time scale of the ionization event (which you calculated in part a), the vibrational wavefunction of the N2 molecule has effectively no time to change. As a result, the newly-formed N_2^+ ion finds itself in a vibrational state which is **not** an eigenfunction of the **new** vibrational Hamiltonian, $\mathbf{H}(N_2^+)$. Assuming that the N_2 molecule was originally in its v=0 vibrational state, calculate the probability that the N_2^+ ion will be produced in its v=0 vibrational state.

Q12

The force constant, k, of the C-O bond in carbon monoxide is $1.87x10^6\dfrac{\text{g}}{\text{sec}^2}$. Assume that the vibrational motion of CO is purely harmonic and use the reduced mass μ = 6.857 amu.

a. Calculate the spacing between vibrational energy levels in this molecule, in units of ergs and cm^{-1}.

b. Calculate the uncertainty in the internuclear distance in this molecule, assuming it is in its ground vibrational level. Use the ground state vibrational wavefunction $(\Psi_{v=0})$, and calculate $\langle x\rangle$, $\langle x^2\rangle$, and $\Delta x=\sqrt{\langle x^2\rangle-\langle x\rangle^2}$.

c. Under what circumstances (i.e. large or small values of k; large or small values of μ) is the uncertainty in internuclear distance large? Can you think of any relationship between this observation and the fact that helium remains a liquid down to absolute zero?

Q13

Suppose you are given a trial wavefunction of the form:

$$\phi = \frac{Z_e^3}{\pi a_0^3} e^{\left(\frac{-Z_e r_1}{a_0}\right)} e^{\left(\frac{-Z_e r_2}{a_0}\right)}$$

to represent the electronic structure of a two-electron ion of nuclear charge Z and suppose that you were also lucky enough to be **given** the variational integral, W, (instead of asking you to derive it!):

$$W = \left(Z_e^2 - 2ZZ_e + \frac{5}{8}Z_e \right) \frac{e^2}{a_0}.$$

a. Find the optimum value of the variational parameter Z_e for an arbitrary nuclear charge Z by setting $\dfrac{dW}{dZ_e} = 0$. Find both the optimal value of Z_e and the resulting value of W.

b. The total energies of some two-electron atoms and ions have been experimentally determined to be:

$$
\begin{array}{llll}
Z & = 1 & H^- & -14.35 eV \\
Z & = 2 & He & -78.98 eV \\
Z & = 3 & Li^+ & -198.02 eV \\
Z & = 4 & Be^{+2} & -371.5 eV \\
Z & = 5 & B^{+3} & -599.3. eV \\
Z & = 6 & C^{+4} & -881.6 eV \\
Z & = 7 & N^{+5} & -1218.3 eV \\
Z & = 8 & O^{+6} & -1609.5 eV
\end{array}
$$

Using your optimized expression for W, calculate the estimated total energy of each of these atoms and ions. Also calculate the percent error in your estimate for each ion. What physical reason explains the decrease in percentage error as Z increases?

c. In 1928, when quantum mechanics was quite young, it was not known whether the isolated, gas-phase hydride ion, H^-, was stable with respect to dissociation into a hydrogen atom and an electron. Compare your estimated total energy for H^- to the ground state energy of a hydrogen atom and an isolated electron (system energy = -13.60 eV), and show that this simple variational calculation erroneously predicts H^- to be unstable. (More complicated variational treatments give a ground state energy of H^- of -14.35 eV, in agreement with experiment.)

Q14

A particle of mass m moves in a one-dimensional potential given by $\mathbf{H} = -\dfrac{\hbar^2}{2m} \dfrac{d^2}{dx^2} + a|x|$, where the absolute value function is defined by |x| = x if x $\geq$ 0 and |x| = -x if x $\leq$ 0.

a. Use the normalized trial wavefunction $\phi = \sqrt[4]{\dfrac{2b}{\pi}} e^{-bx^2}$ to estimate the energy of the ground state of this system, using the variational principle to evaluate W(b).

b. Optimize b to obtain the best approximation to the ground state energy of this system, using a trial function of the form of ϕ, as given above. The numerically calculated exact ground state energy is $0.808616 \sqrt[3]{\hbar^2} \sqrt[3]{m^{-3}} \sqrt[3]{a^2}$. What is the percent error in your value?

Q15

The harmonic oscillator is specified by the Hamiltonian:

$$\mathbf{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2}kx^2.$$

Suppose the ground state solution to this problem were unknown, and that you wish to approximate it using the variational theorem. Choose as your trial wavefunction,

$$\phi = \sqrt{\frac{15}{16}} \sqrt[{-2}]{a^5} \left(a^2 - x^2\right) \text{ for -a} < \text{x} < \text{a}$$

$$\phi = 0 \text{ for } |\text{x}| \geq \text{a}$$

where a is an arbitrary parameter which specifies the range of the wavefunction. Note that ϕ is properly normalized as given.

a. Calculate $\int\limits_{-\infty}^{+\infty} \phi^{\text{*}} \textbf{H} \phi \, dx$ and show it to be given by:

$$\int\limits_{-\infty}^{+\infty} \phi^* \textbf{H} \phi \, dx = \frac{5}{4} \frac{\hbar^2}{ma^2} + \frac{ka^2}{14}.$$

b. Calculate $\int\limits_{-\infty}^{+\infty} \phi^* \textbf{H} \phi \, dx$ for a = b $\sqrt[4]{\dfrac{\hbar^2}{km}}$ with b = 0.2, 0.4, 0.6 0.8, 1.0, 1.5, 2.0, 2.5, 3.0, 4.0, and 5.0, and plot the result.

c. To find the best approximation to the true wavefunction and its energy, find the minimum of $\int\limits_{-\infty}^{+\infty} \phi^* \textbf{H} \phi \, dx$ by setting $\dfrac{d}{da} \int\limits_{-\infty}^{+\infty} \phi^* \textbf{H} \phi \, dx = 0$ and solving for a. Substitute this value into the experssion for $\int\limits_{-\infty}^{+\infty} \phi^* \textbf{H} \phi \, dx$ given in part a. to obtain the best approximation for the energy of the ground state of the harmonic oscillator.

d. What is the percent error in your calculated energy of part c. ?

Q16

Einstein told us that the (relativistic) expression for the energy of a particle having rest mass m and momentum p is $E^2 = m^2 c^4 + p^2 c^2$.

a. Derive an expression for the relativistic kinetic energy operator which contains terms correct through one higher order than the "ordinary" $E = mc^2 + \dfrac{p^2}{2m}$

b. Using the first order correction as a perturbation, compute the first-order perturbation theory estimate of the energy for the 1s level of a hydrogen-like atom (general Z). Show the Z dependence of the result.

$$\text{Note: } \Psi(r)_{1s} = \sqrt{\frac{Z}{a}}^3 \sqrt{\frac{1}{\pi}} e^{-\frac{Zr}{a}} \text{ and } E_{1s} = -\frac{Z^2 me^4}{2\hbar^2}$$

c. For what value of Z does this first-order relativistic correction amount to 10% of the unperturbed (non-relativistic) 1s energy?

Q17

Consider an electron constrained to move on the surface of a sphere of radius r. The Hamiltonian for such motion consists of a kinetic energy term only $\textbf{H}_0 = \dfrac{\textbf{L}^2}{2m_e r_0^2}$, where $\textbf{L}$ is the orbital angular momentum operator involving derivatives with respect to the spherical polar coordinates (θ, ϕ). $\textbf{H}_0$ has the complete set of eigenfunctions $\psi_{lm}^{(0)} = Y_{l,m}(\theta, \phi)$.

a. Compute the zeroth order energy levels of this system.

b. A uniform electric field is applied along the z-axis, introducing a perturbation $V = -e\epsilon z = -e\epsilon r_0 \text{Cos}\theta$, where ϵ is the strength of the field. Evaluate the correction to the energy of the lowest level through second order in perturbation theory, using the identity

$$\text{Cos}\theta Y_{l,m}(\theta, \phi) = \sqrt{\frac{(l+m+1)(l-m+1)}{(2l+1)(2l+3)}} Y_{l+1,m}(\theta, \phi) + \sqrt{\frac{(l+m)(l-m)}{(2l+1)(2l-1)}} Y_{l-1,m}(\theta, \phi).$$

Note that this identity enables you to utilize the orthonormality of the spherical harmonics.

c. The electric polarizability α gives the response of a molecule to an externally applied electric field, and is defined by $\alpha = -\dfrac{\partial^2 E}{\partial^2 \epsilon}\Big|_{\epsilon=0}$ where E is the energy in the presence of the field and ϵ is the strength of the field. Calculate α for this system.

d. Use this problem as a model to estimate the polarizability of a hydrogen atom, where $r_0 = a_0$ = 0.529 Å, and a cesium atom, which has a single 6s electron with $r_0 \approx 2.60$ Å. The corresponding experimental values are α_H = 0.6668 Å^3 and $\alpha_{Cs} = 59.6$Å^3 .

Q18

An electron moving in a conjugated bond framework can be viewed as a particle in a box. An externally applied electric field of strength e interacts with the electron in a fashion described by the perturbation $V = e\epsilon\left(x - \dfrac{L}{2}\right)$, where x is the position of the electron in the box, e is the electron's charge, and L is the length of the box.

a. Compute the first order correction to the energy of the n=1 state and the first order wavefunction for the n=1 state. In the wavefunction calculation, you need only compute the contribution to $\Psi_1^{(1)}$ made by $\Psi_2^{(0)}$. Make a rough (no calculation needed) sketch of $\Psi_1^{(0)} + \Psi_1^{(1)}$ as a function of x and physically interpret the graph.

b. Using your answer to part a. compute the induced dipole moment caused by the polarization of the electron density due to the electric field effect $\mu_{\text{induced}} = -e \int \Psi^* \left(x - \dfrac{L}{2}\right) \Psi dx$. You may neglect the term proportional to ϵ^2; merely obtain the term linear in ϵ.

c. Compute the polarizability, α, of the electron in the n=1 state of the box, and explain physically why α should depend as it does upon the length of the box L. Remember that $\alpha = \left.\dfrac{\partial \mu}{\partial \epsilon}\right|_{\epsilon=0}$.