

5.74, Problem Set #2
Spring 2004
Due Date: March 1, 2004

(For this set, do Problem 1 and either Problem 2 or Problem 3).

1. Consider a two-level system with Hamiltonian:

$$H_0 = |\ell\rangle \varepsilon_\ell \langle \ell| + |k\rangle \varepsilon_k \langle k|$$

A time-dependent potential connects the two levels

$$V(t) = |\ell\rangle V_{lk}(t) \langle k| + |k\rangle V_{kl}(t) \langle \ell|$$
$$V(t) = -\mu E \cos \omega t$$

At time $t=0$, the system is in $|\ell\rangle$. What is the probability of finding it in state $|k\rangle$ at time t ?

- a) Find $P_k(t)$ by exactly solving the coupled differential equations that describe the time-dependent expansion coefficient for these states.
- b) Find $P_k(t)$ using time-dependent perturbation theory to lowest nonvanishing order.
2. **Vibrational Excitation by a Shock Wave.** We are going to study the excitation of higher lying vibrational levels of an anharmonic potential that would occur in a molecular crystal or liquid subjected to a shock wave. A strong shock wave in a molecular crystal could be launched by applying an abrupt pressure of 5 GPa, launching a shock wave that travels at about 5 nm/ps, leading to the compression of a solid by about 20%. The compression can lead to vibrational excitation and heating of molecules in the shock zone, which can induce chemical reactions (like detonation of explosives).

We will study a simplified model that captures the effects of such an excitation. We will partition the Hamiltonian as

$$H = H_0 + V(t) \tag{1}$$

Let's take the vibrational system to be excited, H_0 , to be an anharmonic oscillator with a Morse potential:

$$H_0 = \frac{\hat{p}^2}{2m} + D_e [1 - e^{-\alpha \hat{x}}]^2 \quad (2)$$

Here $\hat{x} = R - R_0$ is a reduced coordinate. We'll treat the shock wave $V(t)$ as a transient compression. The effect of a shock wave would most likely include couplings that deform the potential and also kinetic couplings. Here we will choose the simplest form—the leading term in an expansion—in which the compression wave is linearly coupled to the oscillator

$$V(t) = A \cdot \hat{x} \cdot f(t) \quad (3)$$

Here $f(t)$ is the normalized time-profile of the shock wave and A is an amplitude factor that describes the strength of coupling of the shock wave to the oscillator.

In this problem, we will study the time-dependent excitation of vibrational eigenstates of H_0 by directly numerically solving the coupled linear differential equations that describe the time-evolution of b_n , the expansion coefficients in the eigenstates of H_0 :

$$\frac{\partial b_m(t)}{\partial t} = \frac{-i}{\hbar} \sum_n b_n(t) e^{-i\omega_{nm}t} V_{mn}(t) \quad (4)$$

We will start by (a) calculating the vibrational eigenenergies and wavefunctions for eq. 2, (b) calculate the matrix elements in V , and then (c) numerically solve eqs. 4.

(a) To begin, we need to know the eigenenergies E_n and nuclear wavefunctions $\psi_n(\mathbf{r})$ of our system. We will use the parameters used for H_2 :

$$D_e/hc = 38297 \text{ cm}^{-1}; \alpha = 2\pi\nu_e(\mu/2D_e)^{1/2}; \nu_e/c = 4403.2 \text{ cm}^{-1}; R_e = 0.741 \text{ \AA}.$$

Alumni of 5.73 will be familiar with numerical (or analytic) methods of calculating these and the matrix elements in (b). You should feel free to use any method you're comfortable with. I followed more primitive procedures described in I. N. Levine, *Quantum Chemistry*, 5th ed., Sec. 4.4 and 13.2. This describes a fairly simple routine using a set of reduced variables.

Tabulate the eigenenergies for $v = 0$ to 5, and plot the corresponding nuclear wavefunctions.

(b) Use the results of (a) to calculate the matrix elements $V_{mn}(t)$. Use any method you feel comfortable with. Levine, Sec. 13.2, also describes a numerical approach to this.

Tabulate V_{mn} for $m, n = 0$ to 5.

- (c) For a system initially occupying the ground vibrational state, $b_0(0)=1$, calculate how the system responds when subjected to a Gaussian compression:

$$f(t) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{(t-t_{\text{peak}})^2}{2\sigma^2}\right) \quad (5)$$

where the compression width is $\sigma=2$ fs. (This is a particularly fast shock wave).

Show the time-developing probability of occupying the $v=0$ to 5 states through the course of the shock wave, using an amplitude A that leaves the ground state 90% depleted after the compression. What amplitude is in these states after the compression?

This will require numerically solving the set of six coupled first-order linear differential equations that describe the time-evolution of the expansion coefficients in the $v=0$ to 5 eigenstates. (You can neglect couplings to higher lying states). You will need to numerically integrate the differential equations, probably using a mathematical software package like MatLab or MathCad. Most of these packages have a function call that uses the Runge-Kutta method. Generally speaking these routines require real valued numbers to solve the equations. If so, you will need to separate the real and imaginary parts of each equation, giving 12 coupled differential equations. To see these, expand eq. 4 using $b_k = \text{Re}[b_k] + i \text{Im}[b_k]$, and then separate the real and imaginary variables.

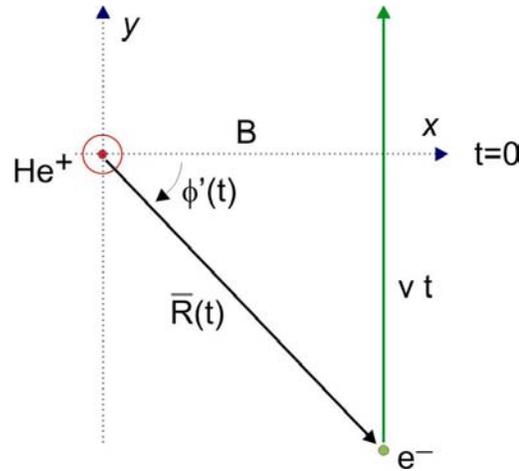
- (d) Plot the time-dependent displacement of the nuclear coordinate, $\langle R(t) \rangle$.
- (e) Show the wavepacket launched by the shock wave, by plotting the probability amplitude for the nuclear wavefunction for the system $P(r,t) = \langle \Psi(r,t) | \Psi(r,t) \rangle$ before, during, and after the compression.
- (f) Estimate the power in the compression pulse.
- (g) Describe the role of the compression pulse width and amplitudes on the efficiency of vibrational up-pumping.

3. **Electronic excitation by electron scattering.**

An electron passes by a He^+ ($Z=2$) atom with a velocity v in the y direction. At the time of closest approach, ($t = 0$), the ion is separated by a distance B (the impact parameter) along the x direction. At any other time, the distance between the atom and electron is

$$R(t) = \sqrt{B^2 + (vt)^2} \quad (6)$$

Through Coulombic interactions as it passes by, the electron will act to mix the electronic states of the atom, which we will take to be real hydrogen-like wavefunctions.



The time dependent Hamiltonian for this problem could be written in terms of the Hamiltonians for the atom and for the electron, as well as a time-dependent interaction between them $H = H_{\text{atom}} + H_{\text{electron}} + V(t)$. Let's consider how a weak interaction mixes the atomic eigenstates. This is an appropriate picture if $|V(t)| \ll |H_{\text{atom}}|$. To just consider the induced changes to the electronic wavefunction of the atom, we will write

$$H = H_{\text{atom}} + V(t) \quad (7)$$

and treat the problem in the interaction picture. We will assume that we prepare the atom at $t = -\infty$ in the $1s$ orbital [$b_{1s}(-\infty) = 1$] and follow time dependent interactions that couple the $1s$ state to the $n = 2$ states. This would hold for relatively large impact parameters, so we will assume that the separation of the free electron from He^+ nucleus and the He^+ electron are approximately equal: $R_{pe} \approx R_{ee} = R(t)$. We can take the frame of reference to be the atomic nucleus.

- Write out an explicit form of the Hamiltonian in eq. 7 in terms of kinetic and potential energies involved. Assume that you can neglect the kinetic energy of the nucleus. Neglect any interactions between the particles other than the Coulomb terms (for instance spin).
- To start, determine the time-dependent matrix elements in the interaction Hamiltonian $V_{ab}(t) = \langle a | V(t) | b \rangle$ where $|a\rangle$ and $|b\rangle$ include the $n=1$ and $n=2$ ($2s, 2px, 2py, 2pz$) states.

To evaluate these matrix elements, we choose the nucleus as the frame of reference and write the problem in terms of spherical coordinates. Write the hydrogenic wavefunctions in terms of spherical harmonics $|a\rangle = \mathbf{R}(r) | \ell m \rangle$. The

matrix elements involve an integral over the wavefunctions for the bound electron position, which are described by coordinates (r, θ, ϕ) . The position of the free (moving) electron is described by the coordinates $(R(t), \theta', \phi'(t))$. It will be necessary to represent the time-dependent potential in terms of an expansion in spherical harmonics, for which the following expression (from Jackson, Classical Electrodynamics) is very helpful:

$$\frac{1}{|\vec{R}(t) - \vec{r}|} = 4\pi \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \frac{1}{2\ell+1} \frac{1}{R(t)} \left(\frac{r}{R(t)} \right)^{\ell} Y_{\ell m}^*(\theta', \phi') Y_{\ell m}(\theta, \phi) \quad (8)$$

Here $\vec{R}(t)$ and \vec{r} are vectors from the nucleus to the electrons, but $R(t)$ and r are scalars.

Evaluate all of the matrix elements. Show their dependence on the impact parameter, the Bohr radius a_0 , electron velocity, and time.

- (c) Using the methods developed in problem 2, numerically solve the coupled differential equations for the time-dependent interactions between the electronic states. Show the time-dependent probabilities of occupying the $n=1$ and $n=2$ states, from large negative times to large positive times. You can take the energy of the $1s$ state to be $E_{n=1}=0$ and the energies of the degenerate $n=2$ states to be $E_{n=2} = 82,000 \text{ cm}^{-1}$. To start, choose $B = 2a_0$. Choose what you would call relatively low or high velocities for these parameters. What time point would effectively constitute $t = -\infty$? Discuss the influence of the velocity and impact parameter on the observed time-dependence.
- (d) Make sequential contour plots of the time-dependent electron probability density in the x - y plane for several times from $t < 0$ to $t > 0$.
- (e) Compare the results in (c) with the results of first order perturbation theory.