

Homework 4

Due Mon Oct 22 at 5:00 pm in Prof. Ginger's mailbox

CIRCLE YOUR ANSWERS AND KEY INTERMEDIATE RESULTS

USE MAPLE WHENEVER POSSIBLE

STAPLE YOUR PAPERS TOGETHER

INCLUDE ALL COMPUTER PRINTOUTS (with commentary)

Levine Problems (5th Ed. in parenthesis) 6th Ed.

(4.16) 4.14 most likely particle position

(4.18) 4.19 3D SHO (note: you don't need to resolve parts we've already solved)

(4.27) 4.25 vibrations in LiH and ICl

(4.29) 4.28 Morse Potential – also: **c)** Given that $D_e = 7.31E-19$ J/molecule, and $a=1.82E10$ m⁻¹ for HCl, calculate the force constant k for the HCl bond. Plot the Morse Potential for HCl and the corresponding Harmonic oscillator potential on the same graph.

d) for what displacements from equilibrium is the harmonic oscillator (HO) potential a good approximation of the Morse potential (*this requires only a qualitative answer*)?

e) For what physical situations would the HO potential yield a poor approximation to the actual potential? (*again, requires a qualitative answer*)

Additional Problems:

1) In lecture we derived the density of states for particle in a 3D box as:

$$D(E) = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} E^{1/2}, \text{ starting with an approximation for the number of states with } n_x^2 + n_y^2$$

$+n_z^2 \leq n^2$ as a function of n . Test this starting approximation by writing a program or routine in Maple (or C or Fortran or Basic or Labview or whatever) to calculate the ACTUAL number of states below the energy corresponding to a given n and compare it to the formula (and calculate % error of the formula) for values of n from $n=1$ to $n=200$ (i.e. $n^2=1$ to 40000).

2) In lecture we introduced the lowering operator as $a^- = \frac{1}{\sqrt{2\hbar\mu\omega}} (+ip + \mu\omega x)$

By arguing that energy can't be negative, we reasoned that there must be some state $|\psi_0\rangle$ for which $a^-|\psi_0\rangle=0$. Use this relationship to generate a first-order differential equation for ψ_0 and solve the resulting differential equation (it should be a "simple" first-order equation) to find ψ_0 . The answer is the same as obtained with the power series solution in Levine.

2) Find ψ_1 , the first excited state of the SHO, by explicitly applying the raising operator, a^+ to ψ_0

3) The frequencies of the three normal modes of H₂O are $\omega_1=3833$ cm⁻¹ $\omega_2=1649$ cm⁻¹ and $\omega_3=3943$ cm⁻¹. If we describe a vibrationally excited state by the notation $(n_1 n_2 n_3)$ where n_i is the quantum number associated with the i^{th} normal mode, what is the energy of the (121) state? What is the energy difference between the (112) and (010) state? Side note not needed for the problem: anharmonicity in real bonds tends to mix the normal modes over time so energy will spread out between the modes.

4) The spatial Parity operator P satisfies the eigenvalue equation: $P \psi = p\psi$ where the eigenvalues of P are $p=+1$ (if ψ is even) and $p=-1$ (if ψ is odd) . Only even and odd functions are eigenfunctions of P . We claimed in lecture that the symmetry of the Hamiltonian has important consequences for the symmetry of the allowed wave functions that we examine below.

4a) Show that if the Hamiltonian is a symmetric (even) function, then $[P,H]=0$ (hint: what is the parity of an even function times an even function, or an odd function times an odd function, i.e. $P(f_1f_2)=?$)

4b) *Two operators will commute if and only if they have a simultaneous set of eigenfunctions.* Use this fact, and your result from a) to justify that statement that “for a symmetric Hamiltonian, the only allowed energy eigenfunctions will be even and odd functions.” The analysis of the spatial symmetry of a wavefunction is a very powerful tool that allows you to predict properties of molecules (i.e. for instance how many IR and Raman active of normal vibrational modes a molecule will have).