PHY 392K (55190) Solid State Physics I, spring 2020

Homework #1

Due February 18, 2020

Problem 1. In the Born Oppenheimer (BO) approximation, we neglected the so-called non-adiabaticity term on the right-hand side and obtained a Schrödinger-like equation for the coefficients of the BO expansion that we interpreted as the proton wave functions in the case of the hydrogen molecule. Derive the expression for the non-adiabaticity operator in the general case of N ionic cores (the core is a combination of the nucleus and all electros not included in the valence shell). What does it look like in the naïve BO approximation?

Problem 2. Consider a hydrogen molecule. Assuming the minimal basis of 1*s* orbitals and two spin states, you can build a basis for the two-electron Hilbert space using either the atomic or the molecular orbital picture.

a) Draw diagrams/cartoons representing the basis states in these two pictures.
b) Write a wave function in the coordinate representation, corresponding to the highest energy state (if there is one) for each of your two basis sets.

Problem 3. Write down the total wave function in the naïve Born-Oppenheimer approximation for a hydrogen molecule in the electronic ground state (minimal 1s basis, you can use either spin orbitals or just factorize the spin wave function), and the first excited ionic rotational and vibrational states. Assume you are in the center of mass reference frame.

Problem 4. Consider a model system: A one dimensional hydrogen dimer (H_2), each atom has one s-state and one electron. Let's use the independent electron approximation, and assume the basis of linear combination of atomic orbitals (LCAO). Assume it is **ORTHOGONAL** for simplicity.

a) ***Construct a Hamiltonian matrix*** of this problem using the LCAO basis (similar to what we did in class; ask me or Ali if you have doubts).
b) ***Find the eigenvalues and eigenvectors*** of the dimer Hamiltonian analytically with the following matrix elements: $\langle 1|H|1\rangle = \varepsilon_0, \langle 1|H|2\rangle = -V$. Make a sketch of the spectrum. Because the electrons are independent, you can just distribute them over the just found spectrum. Remember, that electrons have spin, but it is not included in the Hamiltonian, but you have to use the Pauli principle, and each of your energy levels can take no more than spin up and spin down electrons (tow in total, then it is full!).
c) The electronic contribution to the total energy of a molecule is given by $E_e = \sum_{i=1}^{2} \varepsilon_i$ where the sum runs over all electrons in their corresponding occupied states (do not forget the Pauli principle). Set $\varepsilon_0 = 0$ and $|V| = 2eV$, and ***calculate the electronic total energy***.
d) Now, assume that the matrix element *V* has the following dependence on the inter-atomic distance ***d***: $V = \frac{A}{d^2}$, note that the electronic total energy provides attraction, it gets lower if the distance gets smaller. Then, for the molecule not to collapse, in addition to the electronic energy there should be a purely repulsive term say of the form: $E_{rep} = \frac{B}{d^4}$. ***Find analytically the total energy of a dimer as a function of d, and the equilibrium inter-atomic distance d_0.*** Take A=2 eVÅ^2 and B=2 eVÅ^4 and sketch this energy function.

e) Now, use an ***appropriate numeric technique*** to find the equilibrium inter-atomic distance, which corresponds to the total energy minimum. Compare with the analytic solution. (numerical min value seeking)

f) Find the Taylor expansion of the total energy about the minimum up to second order (harmonic approximation) analytically.

g) Assuming this total energy expression governs the dimer dynamics, ***find the frequency of the dimer vibration*** (make sure you are using the right mass) ***analytically***.

h) ***Calculate and code up the force acting on each atom*** in your model using the full potential, not the harmonic approximation (make sure you take the derivative correctly: $d = |x_1 - x_2|$).

i) ***Write a Molecular Dynamics program*** to study the dynamics of your molecule. ***Hint:*** what should be the time step in your program?

j) Stretch you dimer, and let it vibrate, while collecting the velocity data during the run. ***Compute the velocity-velocity autocorrelation function***:

$$g(t) = \sum_{n=1}^{N} \frac{\langle v_n(t) v_n(0) \rangle}{\langle v_n(0) v_n(0) \rangle},$$

where the brackets indicate the "ensemble average" over two atoms:

$$\langle f(t_i) f(0) \rangle = \frac{1}{M - i + 1} \sum_{m}^{M-1} f(t_{i+m}) f(t_m),$$

where t_j is the time at the j^{th} stem, and M is the total number of steps.

k) ***BONUS QUESTION: Calculate the Fourier cosine transform of g(t)***:

$$g(\omega) = \frac{1}{T} \int_0^T g(t) W(t) \cos(\omega t) dt$$

$$W(t) = 0.42 - 0.5 \cos\left(\frac{\pi t}{t_{\max}}\right) + 0.08 \cos\left(\frac{2\pi t}{t_{\max}}\right)$$

Plot it and describe how many peaks you have and what they correspond to. What is the temperature of your simulation?

Bonus Problem 5

Consider the so-called two site electronic Hubbard model (two sites and two possible values of spin). What is the dimension of the total Hilbert space known as the Fock space, for this problem? The Fock space is the direct sum of individual Hilbert spaces corresponding to zero particle states, one particle states, two particle states, etc.

Consider the Hilbert space for just two electrons (with spin) and two sites, using the following notation $|\uparrow \quad \uparrow\rangle$, $|\uparrow\downarrow \quad 0\rangle$ representing two electrons on two sites (say ***a*** and ***b***) both with spin up (a

ferromagnetic arrangement) and both electrons on site ***a*** (ionic configuration), respectively. Write down all possible basis states.

As you know the position operator has a continues spectrum: $\hat{x}\left|x'\right\rangle = x'\left|x'\right\rangle$.

If you are in a single electron state ***a***, the one electron wave function is simply the inner product $\varphi_a(x) = \langle x|a\rangle$. What is $\left\langle x \quad x'\right|\uparrow \quad \downarrow\rangle$?