
Edlisefnafrædi 1

Lokapróf, 20. desember 2006

Leyfileg hjálpargögn: Reiknivélar og stærdfrædihandbækur
Prófid samanstendur af 4 spurningum sem eru mislangar. Aftast er tafla yfir jöfnur. Mikilvægt er ad rökstydja öll svör.

Spurning 1: (30 punktar)

A hydrogen atom adsorbed on the surface of a metal crystal can be considered as a quantum particle moving in a periodic potential (the metal atoms are considered to be stationary because they are so much heavier than the hydrogen atom). The potential energy of the hydrogen atom can be approximated by the function

$$V(x) = V_s e^{-sin(2\pi x/a)}$$

(a) Sketch (qualitatively) the potential energy function over the interval $(0, a)$. Label the axes, mark the values $x = a$ and $E_{pot} = V_s$, and indicate on the x-axis the locations where the H-atom would sit if it had no kinetic energy and had minimal potential energy.

(b) Derive an expression for the force acting on the hydrogen atom.

(c) Expand $V(x)$ in a Taylor series about one of the minima up to second order in x and give an expression for the force constant, k, of the harmonic oscillator approximation to $V(x)$ in terms of V_s, a and other constants.

(d) What is the value of the zero-point energy of the hydrogen atom within the harmonic approximation described in part (c)?

(e) What would the energy of a photon need to be in order to excite the hydrogen atom from the ground state to the first excited state (assuming the harmonic approximation)?

(f) Given that the hydrogen atom has four bound states in each of the wells in the potential $V(x)$, sketch (qualitatively) the photo-absorption spectrum for the hydrogen atom (taking into account that the harmonic approximation is just a rough, first order approximation that is mainly valid for the lower levels). Explain carefully your reasoning for the relative position and height of the peaks.

Spurning 2: (20 punktar)

Consider a two-dimensional harmonic oscillator with potential energy given by

$$V(x, y) \;=\; ax^2 + by^2$$

(a) Write down an expression for the Hamiltonian operator for this system.

(b) What are the energy levels of the oscillator?

(c) Assume $a = 4b$. Give an expression for the first excited state wave function.

(d) What is the degeneracy of the four lowest energy levels, again assuming $a = 2b$ (sketch an energy level diagram)?

Spurning 3: (20 punktar)

Consider a simple, one-dimensional model for a diatomic molecule. In each of the two atoms, there is a single valence electron and its interaction with the nucleus and the inner electrons can be approximated with a square well potential function. That is, the potential energy function for a valence electron in an atom is $V(x) = -V_0$ when $-a/2 \leq x \leq a/2$ but zero elsewhere. One of the atoms is located at $x = b/2$ and the other one at $x = -b/2$.

(a) Sketch the potential energy function for the electron in a diatomic molecular ion with a charge of +e and write down the Hamiltonian for this system. Invoke the Born Oppenheimer approximation and explain what it involves.

(b) Assume the wavefunction for each atom can be well enough approximated by a single Gaussian function. Invoke the LCAO-MO approximation and derive an expression for the wavefunction and the molecular bond energy of the lowest energy molecular orbital. Simplify the expressions as much as possible. Sketch how the bond energy varies as a function of the distance between the atoms, b. Explain each step in the derivation.

(c) Write down a Slater determinant wavefunction for the ground state of the neutral diatomic molecule (with two valence electrons).

(d) Consider the limit as the two atoms move apart, i.e. b becomes very large. What is the long range form of the single Slater determinant wave function for the two electrons in the neutral diatomic molecule? Discuss the limitation of this approximation and show how it can be improved by using the configuration interaction (CI) method.

Spurning 4: (30 punktar)

(a) Explain what is meant by the self-consistent field (SCF) method for solving the Hartree-Fock equations of a many electron atom or molecule.

(b) Write down a restricted Slater determinant wavefunction for a Li atom corresponding to the electron configuration $1s^2 2s^1$ given that the projection of the total spin on the z-axis is +1/2.

(c) Explain how a Slater determinant form of a many-electron wavefunction is consistent with the Pauli exclusion principle.

(d) Explain what is meant by the 6-31G* basis set in molecular wave function calculations.

(e) Define and explain what is meant by *correlation energy* and state briefly how one could calculate the correlation energy of, for example, an atom.