Lokapróf, maí 2007, endurbætt

Leyfileg hjálpargögn: allt ólífrænt.

Með undirskrift minni hér að neðan staðfesti ég að við úrlausn þessa prófs hefi ég aðeins notið hjálpar ólífrænna hjálpargagna og hefi ekki rætt prófið á nokkurn hátt við aðrar manneskjur

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Undirskrift nemanda

Problem 1: Variational calculation

In this problem the energy and the ground as well as first excited state wave function of a particle in a box with finite walls is estimated using the variational principle. While this problem can be solved exactly, it is instructive to see how well the variational approach with rather simple trial functions can approximate the exact solution.

The potential is:
$$V(x) = \begin{cases} 0 & -a \leq x \leq a \\ V_0 & \text{elsewhere} \end{cases}$$

(a) Approximate the ground state wave function by the simplest even polynomial which goes to zero outside a finite range $x = \pm b$:

$$\psi(x) = \begin{cases} b^2 - x^2 & \text{for} \quad -b \leq x \leq b \\ 0 & \text{elsewhere} \end{cases}$$

(here the family of trial functions depends on the free parameter b). Choose parameters to roughly mimmic the effective potential of the valence electron in a Li atom, $a = 1.55\text{Å}$ and $V_0 = 7.5\ eV$ and calculate a best estimate of the ionization energy. The exact value for the ionization energy of an electron in this square well is 5.7 eV. How well does the variational calculation here agree with this value? Also, calculate how likely it is to find the electron in the classically forbidden region.

(b) Write down an analogous expression for a set of polynomial trial functions where the variational optimization will give an estimate of the first excited state.

Problem 2: Slater determinants

Let ϕ_a, ϕ_b and ϕ_c be three eigenfunctions (orbitals) of a one-electron Hamiltonian

$$h(i) = -\frac{\hbar^2 \nabla_i^2}{2m} + V(i)$$

with non-degenerate eigenvalues w_a, w_b and w_c respectively, i.e.

$$h\phi_a(\vec{r}) = w_a\phi_a(\vec{r}), \quad etc.$$

(a) How many Slater determinants can be formed to describe the state of a four electron system with only one electron in ϕ_b and ϕ_c? (Show each Slater determinant symbolically).

(b) Given the total Hamiltonian

$$H = \sum_{i=1}^{3} h(i) + \sum_{i<j} \frac{e^2}{r_{ij}}$$

evaluate $< \Psi_1|H|\Psi_1 >$ where $|\Psi_1 >$ denotes the $M_s = 1$ state (M_s is the eigenvalue of S_z). Give your answer in terms of w_a, w_b, w_c, J_{ab}, J_{bc}, J_{ca}, K_{ab}, K_{bc} and K_{ca}. Show that your results are consistent with the following rule:

For a determinantal wave function

   I.   each electron in spatial orbital ψ_i contributes h_{ii} to the energy,

   II. each unique pair of electrons contributes J_{ij} (irrespective of spin),

   III. each pair of electons with parallel spin contributes $-K_{ij}$.

(c) Using the rules in part (b), give the energy of one of the $M_s = 0$ determinants from part (a), $|\Psi_0 >$.

(d) Show that $< \Psi_1|H|\Psi_0 >= 0$.

Problem 3: Coupling of two angular momenta

Consider two nuclei with spin angular momenta, $S_1 = 1$ and $S_2 = 1$. (These could be the nuclei of two deuterium atoms).

(a) Write down the direct product basis vectors for the system, $|m_1\ m_2 >$.

Assume now that the two angular momenta are coupled in such a way that an extra term, W, is introduced in the Hamiltonian:

$$W = a\vec{S}_1 \cdot \vec{S}_2.$$

(This could be dipolar coupling between the deuterium nuclei).

(b) In the presence of the coupling W between the two spins, the direction of the S_1 and S_2 vectors changes with time. Derive an expression for the time evolution of the

expectation value of the z-component of both S_1 and S_2 in terms of the coupling constant a and other known quantities.

(c) What are the energy levels of the two spin system and what is their degeneracy?

(d) Give an expression for the stationary states of the system in terms of the direct product basis in part (a).

(e) Assume that at time $t = 0$ the two angular momentum vectors are aligned in the opposite direction, $m_1 = -1$ and $m_2 = 1$. Give an expression (in terms of a) for the state vector after time t. Would it be possible to find some time t_r at which the two spins have reversed completely, i.e. $m_1 = 1$ and $m_2 = -1$. Explain.

Problem 4: Transition state theory and the harmonic approximation

(i) Describe how a variational principle can be derived for the selection of the optimal transition state dividing surface and explain how corrections to the transition state theory approximation to the rate constant can be obtained from classical trajectories.

(ii) A Li atom on the (100) surface of an iron crystal can diffuse over the surface by thermally activated hops between adjacent sites. The atom can be considered to be a particle moving on a periodic, three-dimensional potential energy surface (PES) while the iron atoms are fixed. This is a good approximation since the Li atom is so much lighter than the iron atoms.

The PES can be approximated as

$$V(x, y, z) = V_s \left(e^{-sin(2\pi x/b) - sin(2\pi y/b) - 2\alpha z} - 2e^{-\alpha z} \right).$$

One of the minima is at $(x, y, z) = (b/4, b/4, -2/\alpha)$ and one of the adjacent saddle points is at $(x, y, z) = (b/4, 3b/4, 0)$.

A reasonable approximation is to set $\alpha = 2.0$ Å^{-1}. Then, a second order Taylor expansion of the PES around the minimum is

$$V(x, y, z) = V_s e^2 \left(-1 + 2 \left(\frac{\pi}{b} \right)^2 \left(\left(x - \frac{b}{4} \right)^2 + \left(y - \frac{b}{4} \right)^2 \right) + 4(z + 1)^2 \right)$$

and a similar expansion around the saddle point is

$$V(x, y, z) = V_s \left(-1 + 2 \left(\frac{\pi}{b} \right)^2 \left(\left(x - \frac{b}{4} \right)^2 - \left(y - \frac{3b}{4} \right)^2 \right) + 4z^2 \right).$$

Write down an expression for the rate constant as a function of temperature using the harmonic approximation to TST. Then use the values $V_s = 0.1$ eV and

$b = 2.87\text{Å}$ to simplify the expression as much as possible. Note that $\left(\text{eV}/(\text{amu}\right.$ $\left.\text{Å}^2)\right)^{1/2} = 1.0 \times 10^{14}~\text{s}^{-1}$.

(iii) How long is the time period on average between diffusion hops at room temperature and at 400 K?

(iv) Rewrite the HTST expression for the rate constant to take into account some of the quantum mechanical effects. Do this by introducing the classical partition function for the harmonic oscillator corresponding to each one of the vibrational modes, $q_i = k_B T/\nu_i$ in the HTST expression for the rate constant. Then, replace the classical partition function with a quantum mechanical partition function for each mode. Evaluate the hopping rate using this expression at both room temperature and 400 K and compare with the classical HTST results in part (iii). Discuss what what extent quantum effects have been included with this generalization of the rate constant expression and identify possible quantum mechanical effects that have not been taken into account.