

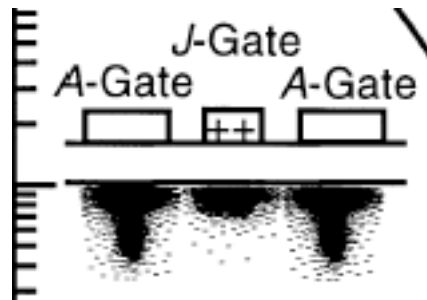
Physics 522. Quantum Mechanics II

Problem Set #7

Due Friday, April 8, 2011

Problem 1: SWAP via the Exchange Interaction (10 Points)

Consider two atoms with a single valence electron, doped into a silicon lattice, but well separated so that each can be treated independently. If a positive bias voltage is applied on a gate the lies between the atoms, the two electron can be made to overlap in a predetermined manner, and previously degenerate singlet and triplet spin states split via the exchange interaction, $\hat{H} = J \vec{s}_1 \cdot \vec{s}_2$, where J is the exchange overlap integral.



From B. E. Kane, "A silicon based nuclear spin quantum computer",
Nature **393**, 133 (1998)

(a) Show that in the uncoupled basis for the two spins, $\{|\uparrow\uparrow\rangle, |\uparrow\downarrow\rangle, |\downarrow\uparrow\rangle, |\downarrow\downarrow\rangle\}$, the matrix representation

$$\hat{H} \doteq \frac{J}{4} \begin{bmatrix} 1 & & & \\ & -1 & 2 & \\ & 2 & -1 & \\ & & & 1 \end{bmatrix}.$$

(b) If overlap is made to occur for a time t show that the two-spin system evolves according to the unitary matrix (in the order basis above)

$$\hat{U}(\theta) \doteq \begin{bmatrix} e^{-i\theta/4} & & & \\ & e^{i\theta/4} \begin{bmatrix} \cos(\theta/2) & -i\sin(\theta/2) \\ -i\sin(\theta/2) & \cos(\theta/2) \end{bmatrix} & & \\ & & & \\ & & & e^{-i\theta/4} \end{bmatrix} \text{ where } \theta = Jt/\hbar.$$

(c) Show that for $\theta=\pi$, the unitary transformation is the "SWAP" operation on the quantum state of the two spins,

$$\hat{U}(\pi)|\psi_1\rangle \otimes |\psi_2\rangle = |\psi_2\rangle \otimes |\psi_1\rangle \text{ (up to an overall phase),}$$

$$\text{where } |\psi_i\rangle = \alpha_i |\uparrow\rangle_i + \beta_i |\downarrow\rangle_i$$

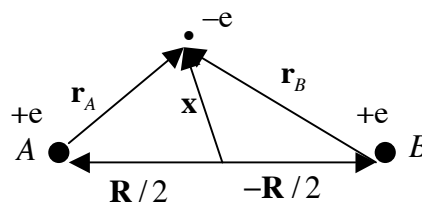
This is an example of “quantum logic”.

Note, when $\theta = \pi/2$ we obtain $\sqrt{\text{SWAP}}$ which generally leaves the two spin state entangled

(c) How does the SWAP defined here differ from the exchange-permutation operator defined in class? For two electrons, we expect the exchange to lead to a phase of negative one, whereas for the SWAP logic gate, there is no such phase?

Problem 2: Diatomic Molecules Encore (20 Points)

The simplest molecule is the hydrogen molecular ion, H_2^+ , consisting of two protons and one electron,



Because the protons are 2000 times heavier than the electrons, it is appropriate to make the *Born-Oppenheimer* approximation: take the nuclei as fixed in space (i.e. treat their position as a classical parameter) and calculate the energy eigenstates of the electrons (here only one electron). The nuclei are then allowed to move in the potential of the resulting electron cloud, with the electrons adjusting adiabatically as a function of \mathbf{R} .

The B-O Hamiltonian is,

$$\hat{H} = \frac{\hat{p}^2}{2m} - \frac{e^2}{\hat{r}_A} - \frac{e^2}{\hat{r}_B} + \frac{e^2}{R},$$

where p is the electron momentum, m its mass, and R (the internuclear separation) is a parameter.

(a) We seek the ground state electronic levels as a function of R . The electron wave function is known as a “molecular orbital”. The problem can be solved exactly using elliptical coordinates. We will use here the approximate variational method. The potential presented by the nuclei to the electron is a three dimensional analog of a “double-well” potential in 1D: the electron can be bound to either proton or “tunnel” between them. Thus, we take as our trial ground state wave function,

$$\tilde{\psi}(\mathbf{x}) = c_A \psi_A(\mathbf{x}) + c_B \psi_B(\mathbf{x}),$$

where $\psi_{A(B)}(\mathbf{x}) = \phi_{1s}(\mathbf{x} \mp \mathbf{R}/2)$ are the hydrogen atom ground states centered at the two nuclei, and the probability amplitudes are real.

Use the variational method to show that there are two possible minima for the ground states according to $c_A = \pm c_B$. We of course could have seen this -- these are the symmetric and antisymmetric (gerade/ungerade) solutions of the double well -- the exercise demonstrates the power of the variational method if the right guess is made. Show that the electronic energy level (molecular potential seen by the nuclei) are

$$E(1\sigma_{g(u)}) = E_{g(u)} + \frac{e^2}{R}, \text{ where } E_{g(u)} = E_H(1s) + \frac{I \pm M}{1 \pm P_{AB}}$$

Here $E_H(1s) = -13.6 \text{ eV}$ is the hydrogen atom 1s binding energy,

$$I = \int d^3x |\psi_A(\mathbf{x})|^2 \left(-\frac{e^2}{r_B} \right) = \frac{e^2}{a_0} \left(-\frac{1}{\bar{R}} + e^{-2\bar{R}} \left(1 + \frac{1}{\bar{R}} \right) \right) < 0 \text{ ("Coulomb integral")}$$

$$M = \int d^3x \psi_A(\mathbf{x}) \left(-\frac{e^2}{r_B} \right) \psi_B(\mathbf{x}) = -\frac{e^2}{a_0} e^{-\bar{R}} (1 + \bar{R}) < 0 \text{ ("Resonance integral")}$$

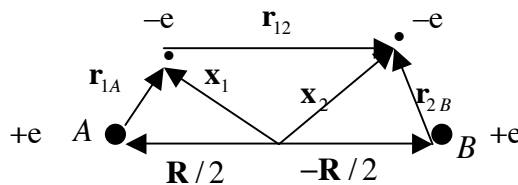
$$P_{AB} = \int d^3x \psi_A(\mathbf{x}) \psi_B(\mathbf{x}) = e^{-\bar{R}} (1 + \bar{R} + \bar{R}^2/3), \text{ with } \bar{R} = R/a_0,$$

and I have introduced the molecular orbital spectroscopic notation: $1\sigma_g \rightarrow$ principal quantum number $n=1$, angular momentum $l_z=0$ about internuclear axis (σ state), and symmetric w.r.t. electron parity (gerade). You need not calculate the integrals above.

(b) Plot the molecular potentials $E(1\sigma_{g(u)})$ as a function of R . Show that the $1\sigma_g$ state allows binding of the two nuclei (i.e. there is a potential well in which the nuclei move). This is simplest example of covalent chemical bond due to the attraction of the nuclei to the shared electron cloud. Estimate the binding energy and equilibrium separation of the nuclei. The exact values are $E_{bind} = 2.79 \text{ eV}$, $\Delta R_{eq} = 2.0 a_0$.

Note: This model underestimates the binding due to the choice of variational wave function. A more sophisticated choice would include the change in the atomic orbitals as the nuclei merge to form a Helium-like charge.

Now consider the simplest *neutral* molecule, diatomic hydrogen H_2 .



The B-O Hamiltonian for this two electron system is

$$\hat{H} = \frac{\hat{p}_1^2}{2m} - \frac{e^2}{r_{1A}} - \frac{e^2}{r_{1B}} + \frac{\hat{p}_2^2}{2m} - \frac{e^2}{r_{2A}} - \frac{e^2}{r_{2B}} + \frac{e^2}{r_{12}} + \frac{e^2}{R}.$$

(c) One approach to finding the energy levels is to build up single electron “molecular orbitals” in the same way as we can build, e.g. atomic Helium, out of single electron hydrogenic orbitals. An alternative approach (the Heitler-London model) is to consider the problem as two interacting hydrogen *atoms*, and treat everything else (interaction of electron 1 with nucleus B, interaction of electron 2 with nucleus A, and interaction of the two electrons) as a perturbation. We thus take as our trial wave function

$\tilde{\psi}(\mathbf{x}_1, \mathbf{x}_2) = c_1 \psi_A(\mathbf{x}_1)\psi_B(\mathbf{x}_2) + c_2 \psi_A(\mathbf{x}_2)\psi_B(\mathbf{x}_1)$ (state with electron 1 in hydrogen atom at proton A and electron 2 in hydrogen atom at proton B, superposed with 1 \leftrightarrow 2).

Show that the variational method gives binding and anti-binding molecular potentials arising from the two electrons

$$E_{\Sigma_g(u)} = 2E(1s) + \frac{2I + K \pm 2MP_{AB} \pm J}{1 \pm P_{AB}^2} + \frac{e^2}{R},$$

where $K = \int d^3x_1 d^3x_2 |\psi_A(\mathbf{x}_1)\psi_B(\mathbf{x}_2)|^2 \frac{e^2}{r_{12}}$ is the “direct term”,

$J = \int d^3x_1 d^3x_2 \psi_A^*(\mathbf{x}_1)\psi_B^*(\mathbf{x}_2) \frac{e^2}{r_{12}} \psi_A(\mathbf{x}_2)\psi_B(\mathbf{x}_1)$ is the “exchange integral”,

with two electron wave functions,

$$\tilde{\psi}_{\Sigma_g(u)}(\mathbf{x}_1, \mathbf{x}_2) = \psi_A(\mathbf{x}_1)\psi_B(\mathbf{x}_2) \pm \psi_A(\mathbf{x}_2)\psi_B(\mathbf{x}_1) \text{ (unnormalized).}$$

Here I have used the molecular “term notation”, where Σ denotes that $L_z=0$ is the *total* angular momentum of the two electrons. his model gives an equilibrium separation of the bond hydrogen molecule as $\Delta R_{eq} = 0.73a_0$, and the binding energy as $E_{bind} = 9.6 eV$

Note: The Heitler-London model assumes as $R \rightarrow \infty$, the molecular energy asymptotes to the energy of two free neutral hydrogen atoms. It neglects possibilities of ionic interactions (i.e. H_2^+ + proton). The molecular orbital model treats these equally. Neither is a very good approximation. A better approximation would use the variational method to optimize these two contributions.

(e) The Pauli principle insists on complete antisymmetry of the two-electron wave function. If we write the total electron state, including spin, **argue** that the “binding state” is $^1\Sigma_g$ (singlet) and the antibinding state is $^3\Sigma_u$ (triplet). **Further argue** why you expect, *physically*, that the singlet provides a binding potential for the nuclei and the triplet an anti-binding potential.