Phys 223B: Condensed Matter Physics, Winter 2016
Problem Set 1 Solutions

from Jennifer Cano

I. HUNDS RULES

(a) First consider $n \leq 2l + 1$. Then Hund's first rule tells us the all the spins will align, yielding $S = \frac{n}{2}$. Hund's second rule tells us to maximize L, hence, $L = l + (l - 1) + (l - 2) + ... + (l - (n - 1)) = \frac{n}{2}(2l - n + 1) = S|2l + 1 - n|$. Hund's third rule tells us that $J = |L - S| = S|1 - (2l - n + 1)| = S|n - 2l|$. So we have the desired result in this case. Next consider $n > 2l + 1$. Hund's first rule tell us that the first $2l + 1$ spins will align and the remaining $n - (2l + 1)$ will anti-align, yielding $S = \frac{1}{2}(2l + 1 - (n - (2l + 1))) = \frac{1}{2}(2(2l + 1) - n)$. Hund's second rule tells us to maximize L, yielding $L = l + (l - 1) + (l - 2) + ... + (l - (n - (2l + 1) - 1)) = (n - (2l + 1))(2l + 1 - \frac{n}{2}) = S|2l + 1 - n|$. Hund's third rule tells us $J = L + S = S(1 + n - (2l + 1)) = S|n - 2l|$.

(b) First consider $L \geq S$. Then the RHS evaluates to:

$$\sum_{J=L-S}^{L+S} (2J + 1) = \sum_{k=0}^{2S} (2(k + L - S) + 1) = (2S + 1)(1 + 2(L - S)) + (2S)(2S + 1) = (2S + 1)(2L + 1) \qquad (1)$$

By exchanging L and S, we get the same result when $L < S$.

(c) Rewrite the spin-orbit interaction: $\lambda(\vec{L} \cdot \vec{S}) = \frac{\lambda}{2}(J^2 - L^2 - S^2)$. In a particular LS-multiplet, L and S are fixed, but J varies from $L + S$ to $|L - S|$. Thus, the splitting within the multiplet is given by

$$E_{J=L+S} - E_{J=|L-S|} = \frac{\lambda}{2}((L + S)(L + S + 1) - |L - S|(|L - S| + 1)) = \frac{\lambda}{2}(4LS + L + S - |L - S|), \qquad (2)$$

which yields $\lambda S(2L + 1)$ when $L > S$ and $\lambda L(2S + 1)$ if $L < S$. The splitting between success J-multiplets within the LS-multiplet is given by $E_{J+1} - E_J = \frac{\lambda}{2}((J + 1)(J + 2) - J(J + 1)) = \lambda(J + 1)$.

II. CRYSTAL FIELD EFFECTS

Rewrite the crystal field term in terms of the raising and lowering operators $L_\pm = L_x \pm iL_y$:

$$H_{\text{crys}} = aL_x^2 + bL_y^2 + cL_z^2 = a\left(\frac{L_+ + L_-}{2}\right)^2 + b\left(\frac{L_+ - L_-}{2i}\right)^2 + cL_z^2 = \frac{a - b}{4}(L_+^2 + L_-^2) + \frac{a + b}{4}(L_+L_- + L_-L_+) + cL_z^2 \quad (3)$$

The $(2L + 1)(2S + 1)$-fold degenerate set of eigenstates can be labelled by their S_z and L_z eigenvalues; since spin does not enter in H_{crys}, it is already diagonal in the S_z basis, so we need only label states by their L_z eigenvalue. In the case where $L = 1$, these states have $L_z = -1, 0$, or 1. We label the corresponding eigenstates $|-\rangle, |0\rangle, |+\rangle$. We want to diagonalize H_{crys} in this basis to do degenerate perturbation theory. Hence, we compute:

$$H_{\text{crys}}|-\rangle = \left(\frac{a - b}{2}\right)|+\rangle + \left(\frac{a + b}{2} + c\right)|-\rangle$$

$$H_{\text{crys}}|+\rangle = \left(\frac{a - b}{2}\right)|-\rangle + \left(\frac{a + b}{2} + c\right)|+\rangle$$

$$H_{\text{crys}}|0\rangle = (a + b)|0\rangle \qquad (4)$$

where we have used $L_+^2|-\rangle = 2|+\rangle, L_-^2|+\rangle = 2|-\rangle, L_\pm L_\mp|\pm\rangle = 2|\pm\rangle, L_\pm L_\mp|0\rangle = 2|0\rangle, L_z^2|m\rangle = m^2|m\rangle$ and the fact that all other states are annihilated by the operators in H_{crys}. From Eq (4), we can see that the eigenstates of H_{crys} are $\frac{1}{\sqrt{2}}(|+\rangle + |-\rangle), \frac{1}{\sqrt{2}}(|+\rangle - |-\rangle)$ and $|0\rangle$, with respective (non-degenerate) energies $a + c, b + c$ and $a + b$.

It remains to show that all matrix elements of $\vec{L}$ vanish in these states:

$$\left(\langle+|\pm\langle-|\right)L_+\left(|+\rangle\pm|-\rangle\right)\propto\left(\langle+|\pm\langle-|\right)|0\rangle=0 \tag{5}$$

$$\left(\langle+|\pm\langle-|\right)L_-\left(|+\rangle\pm|-\rangle\right)\propto\left(\langle+|\pm\langle-|\right)|0\rangle=0 \tag{6}$$

$$\left(\langle+|\pm\langle-|\right)L_z\left(|+\rangle\pm|-\rangle\right)=\left(\langle+|\pm\langle-|\right)\left(|+\rangle\mp|-\rangle\right)=0 \tag{7}$$

$$\langle0|L_\pm|0\rangle\propto\langle0|\pm\rangle=0,\ \langle0|L_z|0\rangle=0 \tag{8}$$

III. SINGLET GROUND STATE OF THE (SPIN-INDEPENDENT) TWO ELECTRON HAMILTONIAN

(a) Because the Hamiltonian is spin-independent, the total wave function can be written as a product of a spatial wave function and a spin wave function. Because the total wave function must be antisymmetric under exchange of the two electrons, symmetric spatial wave functions are antisymmetric under exchanging spins, and thus must have the spins in the singlet state. Similarly, antisymmetric spatial wave functions must have the spins in one of the triplet states. Using the variational principle, $E \geq E_t$ when restricted to antisymmetric spatial wave functions, while $E \geq E_s$ when restricted to spatial wave functions.

(b) It is reasonable to take V real; thus, we are given that ψ_t is real. Consequently, $|\psi_t| = \pm\psi_t$, depending on the sign of ψ_t, and $|\nabla_i\psi_t| = |\nabla_i|\psi_t||$, except at the nodes, where there is a discontinuity in $\nabla_i|\psi_t|$; however, these isolated points should not contribute to the full integral. Thus, $E(|\psi_t|) = E(\psi_t) \equiv E_t$. But we know from part (a) that $E(|\psi_t|) \geq E_s$ because $|\psi_t|$ is symmetric. Thus, $E_s \leq E_t$.

IV. HUBBARD MODEL OF THE HYDROGEN MOLECULE

(a) The problem statement provides us with the Hamiltonian in the $|\mathbf{R}\rangle, |\mathbf{R'}\rangle$ basis:

$$h = \begin{pmatrix} \epsilon & -t \\ -t & \epsilon \end{pmatrix} \tag{9}$$

From the symmetry of this matrix, it is easy to check that the eigenstates are $\frac{1}{\sqrt{2}}\left(|\mathbf{R}\rangle \pm |\mathbf{R'}\rangle\right)$ with energies $\epsilon \mp t$.

(b) The crudest approximation of the two-electron ground state is to put both electrons in the single-electron ground state, $\frac{1}{\sqrt{2}}\left(|\mathbf{R}\rangle + |\mathbf{R'}\rangle\right)$. Not accounting for electron-electron interactions, the energy of this state is $2(\epsilon - t)$. We can estimate the effect of interactions by adding an energy penalty U when both electrons are on the same proton. In this state, the probability that both electrons are on the same proton is the sum of the probability that both electrons are at $\mathbf{R}$ with the probability that both are at $\mathbf{R'}$. Since each probability is $\left(\frac{1}{2}\right)^2 = \frac{1}{4}$, the total probability that both electrons are on the same proton is $\frac{1}{4} + \frac{1}{4} = \frac{1}{2}$. Hence, this logic estimates the ground state energy to be $2(\epsilon - t) + \frac{U}{2}$.

(c) The full set of spatially symmetric (singlet) two-electron states is spanned by the basis states: $\Phi_0 = \frac{1}{\sqrt{2}}\left(|\mathbf{R}\rangle|\mathbf{R'}\rangle + |\mathbf{R'}\rangle|\mathbf{R}\rangle\right)$, $\Phi_1 = |\mathbf{R}\rangle|\mathbf{R}\rangle, \Phi_2 = |\mathbf{R'}\rangle|\mathbf{R'}\rangle$. We can rewrite the estimated state from the previous section in terms of these states as:

$$\Phi_{\text{ie}} \equiv \frac{1}{2}\left(|\mathbf{R}\rangle + |\mathbf{R'}\rangle\right)\left(|\mathbf{R}\rangle + |\mathbf{R'}\rangle\right) = \frac{\Phi_0}{\sqrt{2}} + \frac{1}{2}\left(\Phi_1 + \Phi_2\right) \tag{10}$$

We can compute the total Hamiltonian H in the basis of symmetric states, Φ_0, Φ_1, Φ_2: first, noting that in Φ_1 and Φ_2, there is a 100% chance that both electrons are on the same atom, while in Φ_0 there is a 0% chance, we compute the diagonal entries: $H_{00} = 2\epsilon, H_{11} = H_{22} = 2\epsilon + U$. The off-diagonal entries are computed by considering electron hopping: the single-electron hopping operator is given by $H_{\text{hop}} = -t|\mathbf{R}\rangle\langle\mathbf{R'}| + h.c.$. Thus, matrix elements of the two-electron are given by, for example, $H_{10} = \langle\mathbf{R}|\langle\mathbf{R}|\left(-t|\mathbf{R}\rangle\langle\mathbf{R'}| \otimes \mathbb{I} - t\mathbb{I} \otimes |\mathbf{R}\rangle\langle\mathbf{R'}|\right)\frac{1}{\sqrt{2}}\left(|\mathbf{R}\rangle|\mathbf{R'}\rangle + |\mathbf{R'}\rangle|\mathbf{R}\rangle\right) = -\sqrt{2}t$. By symmetry and Hermiticity, $H_{01} = H_{10} = H_{02} = H_{20}$. The remaining matrix elements are $H_{12} = H_{21} = 0$ because there is no term that simultaneously

hops both electrons. We have verified Eq (32.38) in Ashcroft & Mermin.

(d) The eigenvalues of this Hamiltonian are $2\epsilon + U, 2\epsilon + \frac{1}{2}U \pm \sqrt{4t^2 + \frac{1}{4}U^2}$. Thus, the ground state energy is $2\epsilon + \frac{1}{2}U - \sqrt{4t^2 + \frac{1}{4}U^2}$. Below, we plot this ground state energy compared to the Heitler-London approximation and the independent electron approximation, setting $\epsilon = 0$ to fix the overall energy shift. We can see that there are two regimes: when $U \leq t$, the independent electron approximation approximates the full two-electron approximation to leading (linear) order; this makes sense because when U is small, the Coulomb repulsion is small and the electrons don't see each other, which is exactly the single-electron approximation. On the other hand, when $U \gg t$, the two electron energy asymptotes to 2ϵ and is independent of t. This makes sense because when U is large, the Coulomb repulsion dominates and the electrons do not want to be on the same site; this is exactly the Heitler-London ground state. When $U = 2t$, the independent electron approximation is a better approximation than the Heitler-London to the full two electron energy.
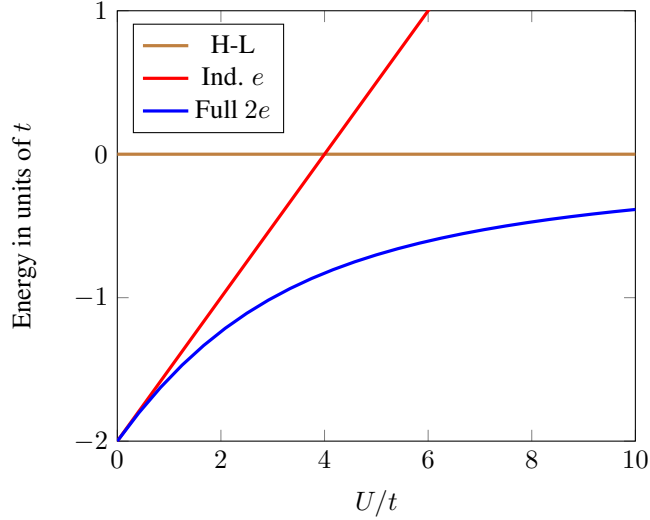
(e) The ground state we find from diagonalizing (32.38) in Mathematica is $\left(\frac{\sqrt{16t^2+U^2}+U}{2\sqrt{2}t}, 1, 1 \right)$ in the basis (Φ_0, Φ_1, Φ_2). We can rewrite this to look like the form in Ashcroft & Mermin by inverting $\left(\frac{\sqrt{16t^2+U^2}+U}{2t} \right)^{-1} = \frac{2t}{\sqrt{16t^2+U^2}+U} = \frac{2t(\sqrt{16t^2+U^2}-U)}{16t^2} = -\frac{U}{8t} + \frac{1}{2}\sqrt{1 + \frac{U^2}{16t^2}}$. The probability of finding two electrons on the same ion is the sum of the probabilities to be in Φ_1 and Φ_2, which is $2\frac{1^2}{\frac{U(\sqrt{16t^2+U^2}+U)}{4t^2}+4} = \frac{8t^2}{U(\sqrt{16t^2+U^2}+U)+16t^2} = \frac{1}{2x(\sqrt{1+x^2}+x)+2} = \frac{1}{2}\left(1 - \frac{x}{\sqrt{1+x^2}} \right)$, where we have defined $x = U/4t$. As $U \to 0$, the probability goes to $1/2$, consistent with what we found in the independent electron approximation, and as $U \to \infty$, the probability goes to zero, consistent with the Heitler-London approximation.
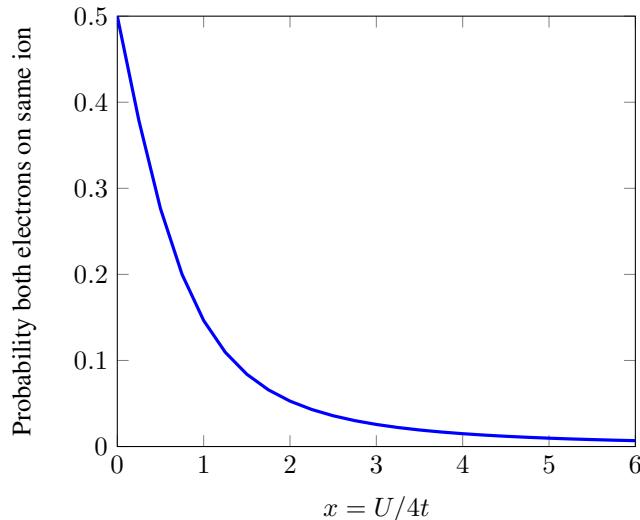
(f) The unique spatially antisymmetric eigenstate of the two-electron problem is $\Phi_t \equiv \frac{1}{\sqrt{2}}\left(|\mathbf{R}\rangle|\mathbf{R'}\rangle - |\mathbf{R'}\rangle|\mathbf{R}\rangle\right)$. Since the hopping term annihilates this state, t does not enter its energy and because the two electrons are never on the same site, U does not enter. Thus, the energy is 2ϵ, the sum of the single-electron energies.

(g) In the limit $U \gg t$, the Coulomb repulsion dominates and we expect to be in a regime where there is only one electron per site; the only two spatial states which meet this requirement are the singlet state Φ_0 and the triplet state. From part (d), expanding the square root to leading order yields the energies for the singlet states, $U, U + J$ and $E_s \equiv -J$, while from part (e), the energy of the triplet state is $E_t \equiv 0$; we have subtracted an overall shift of 2ϵ from each energy and defined $J = \frac{4t^2}{U} > 0$. Thus, the low energy manifold consists of Φ_0 and the three degenerate triplet states with spatial wave function Φ_t. We can always describe a four-level quantum system with two pseudospin-1/2 operators. In this case, since three states are degenerate at energy zero and one state has energy $-J$, the Hamiltonian is a projector onto that one state. In terms of spin language, the operator that projects onto a single state is the (pseudo)spin singlet projector, $-\frac{1}{2}S^2 + 1$. Defining $S = S_\mathbf{R} + S_\mathbf{R'}$ yields the Hamiltonian

$H = -J(-\frac{1}{2}S^2 + 1) = -J\left(-\frac{1}{2}\left(S_\mathbf{R} + S_\mathbf{R'}\right)^2 + 1\right) = JS_\mathbf{R} \cdot S_\mathbf{R'} - \frac{J}{4}$, where we have used $S_\mathbf{R}^2 = S_\mathbf{R'}^2 = \frac{3}{4}$.

Before taking the large-U/t limit, we can compute the difference between the triplet and singlet states: $\Delta E = -\frac{1}{2}U + \sqrt{4t^2 + \frac{1}{4}U^2}$. Below we plot this compared to $J \equiv \frac{4t^2}{U}$ and see that they converge in the large-U/t limit: