

PC4902: Elements of QMBT, Pt 2 Problems 1

Key: **E**asy; **M**oderate; **D**ifficult

- [M] A hydrogen molecule consists of identical hydrogen atoms A and B, each of which has only one electron. We would like to see explicitly how the repulsive interaction between the electrons affects the energy spectrum. To investigate this, consider the following model Hamiltonian

$$\hat{H} = -t \sum_{\sigma} (\hat{c}_{a\sigma}^{\dagger} \hat{c}_{b\sigma} + \hat{c}_{b\sigma}^{\dagger} \hat{c}_{a\sigma}) + U (\hat{c}_{a\uparrow}^{\dagger} \hat{c}_{a\uparrow} \hat{c}_{a\downarrow}^{\dagger} \hat{c}_{a\downarrow} + \hat{c}_{b\uparrow}^{\dagger} \hat{c}_{b\uparrow} \hat{c}_{b\downarrow}^{\dagger} \hat{c}_{b\downarrow}),$$

where, for example, $\hat{c}_{a\sigma}^{\dagger}$ and $\hat{c}_{a\sigma}$ are the creation and annihilation operators for an electron with spin σ on atom A, t is the amplitude for tunnelling of an electron from one atom to the other and U is the electrostatic energy of interaction of the two electrons when they are on the same atom. This \hat{H} , when generalized to describe electrons in a crystal lattice, is normally known as the *Hubbard model* Hamiltonian. In lectures, the Hartree–Fock approximation was used to investigate this model, but it is actually no harder to solve the two-electron problem *exactly*: the Hamiltonian is invariant under a rotation of the spins, so that the eigenstates can be labelled by the total spin, $S = 0$ or 1 ; this fact greatly simplifies the analysis.

If $| \rangle$ denotes the state with no electrons, one of the two-electron *spin triplet* states is $\hat{c}_{a\uparrow}^{\dagger} \hat{c}_{b\uparrow}^{\dagger} | \rangle$. Verify that this [Hartree–Fock] state is an energy eigenstate, and that it corresponds to zero energy. Write down expressions for the other two states of the triplet. These have the same energy, of course.

An orthonormal set of two-electron states with $S = 0$ is

$$|1\rangle = \frac{1}{\sqrt{2}} (\hat{c}_{a\uparrow}^{\dagger} \hat{c}_{b\downarrow}^{\dagger} - \hat{c}_{a\downarrow}^{\dagger} \hat{c}_{b\uparrow}^{\dagger}) | \rangle, \quad |2\rangle = \hat{c}_{a\downarrow}^{\dagger} \hat{c}_{a\uparrow}^{\dagger} | \rangle \quad \text{and} \quad |3\rangle = \hat{c}_{b\downarrow}^{\dagger} \hat{c}_{b\uparrow}^{\dagger} | \rangle.$$

Find the results of applying \hat{H} to each of the above three states, and express your answers as linear combinations of $|1\rangle$, $|2\rangle$ and $|3\rangle$.

Use your results to show that the Hamiltonian matrix \mathbf{H} , with elements $\langle i | \hat{H} | j \rangle$, is

$$\mathbf{H} = \begin{pmatrix} 0 & \sqrt{2}t & \sqrt{2}t \\ \sqrt{2}t & U & 0 \\ \sqrt{2}t & 0 & U \end{pmatrix}.$$

Find the eigenvalues of \mathbf{H} , and hence show that the possible values of the energy for the singlet states are

$$E = U \quad \text{and} \quad \frac{1}{2}U \pm \frac{1}{2}\sqrt{U^2 + 16t^2}.$$

Sketch the ground-state energy $E_0 = \frac{1}{2}U - \frac{1}{2}\sqrt{U^2 + 16t^2}$ as a function of t , regarding U as fixed. Try to interpret the results physically; i.e., consider how you would expect the electron–electron interaction to affect the probability of finding both electrons on the same atom.

Compare this result for E_0 with the results obtained from the Hartree–Fock approximation:

$$E_0 = -2t^2/U \quad \text{for } t < \frac{1}{2}U \quad \text{and} \quad E_0 = -2t + \frac{1}{2}U \quad \text{for } t \geq \frac{1}{2}U.$$

From the variational theorem for the ground-state energy, the Hartree–Fock approximation to E_0 must always be greater than the exact result. Show this explicitly from the above results.