

Heisenberg Hamiltonian (32.20)), one must still face the task of extracting information of physical interest from the model. In general this turns out to be as difficult, subtle, and fascinating as the problem of deriving the model in the first place. A view of this aspect of magnetism is given in Chapter 33.

PROBLEMS

1. *Symmetry of Two-Electron Orbital Wave Functions*

Prove that the stationary states of the orbital Schrödinger equation for a two-electron system with a symmetric potential—i.e., Eq. (32.3) with $V(\mathbf{r}_1, \mathbf{r}_2) = V(\mathbf{r}_2, \mathbf{r}_1)$ —can be chosen to be either symmetric or antisymmetric. (The proof is quite analogous to the first proof of Bloch's theorem in Chapter 8.)

2. *Proof That the Two-Electron Ground State of a Spin-Independent Hamiltonian Is a Singlet*

(a) The mean energy of a two-electron system with Hamiltonian (32.3) in the state ψ can be written (after an integration by parts in the kinetic energy term) in the form:

$$E = \int d\mathbf{r}_1 d\mathbf{r}_2 \left[\frac{\hbar^2}{2m} \{ |\nabla_1 \psi|^2 + |\nabla_2 \psi|^2 \} + V(\mathbf{r}_1, \mathbf{r}_2) |\psi|^2 \right] \quad (32.28)$$

Show that the lowest value (32.28) assumes over all normalized antisymmetric differentiable wave functions ψ that vanish at infinity is the triplet ground-state energy E_t , and that when symmetric functions are used the lowest value is the singlet ground-state energy E_s .

(b) Using (i) the result of (a), (ii) the fact that the triplet ground state ψ_t can be taken to be real when V is real, and (iii) the fact that $|\psi_t|$ is symmetric, deduce that $E_s \leq E_t$.

3. *Symmetry of One-Electron Orbital Wave Functions for the Hydrogen Molecule*

Prove (in much the same way as in Problem 1) that if a one-electron potential has a plane of mirror symmetry, then the stationary one-electron levels can be chosen so that they are either invariant or change sign under reflection in that plane. (This establishes that Eq. (32.11) gives the correct linear combinations of atomic orbitals for the two-proton potential.)

4. *Heitler-London Singlet-Triplet Splitting*

Derive the Heitler-London estimate (32.16) for the difference in singlet and triplet ground-state energies for the hydrogen molecule. (In showing that (32.15) reduces to (32.16) for well-separated protons, it is essential to take into account the following points: (a) The one-electron wave functions ϕ_1 and ϕ_2 out of which (32.13) and (32.14) are constructed are exact ground-state wave functions for a single electron in a hydrogen atom at \mathbf{R}_1 and \mathbf{R}_2 , respectively. (b) The criterion for well-separated protons is that they be far apart compared with the range of a one-electron hydrogenic wave function. (c) The electrostatic field outside of a spherically symmetric distribution of charge is precisely the field one would have if all the charge were concentrated in a single point charge at the center of the sphere. It is also convenient to include in the Hamiltonian the (constant) interaction energy $e^2/|\mathbf{R}_1 - \mathbf{R}_2|$ of the two protons.)

5. *Hubbard Model of the Hydrogen Molecule*

The Hubbard model represents an atom at \mathbf{R} by a single orbital electronic level $|\mathbf{R}\rangle$. If the level is empty (no electron on the atom) the energy is zero, if one electron (of either spin) is in the level the energy is ε , and if two electrons (of necessarily opposite spins) are in the level the energy

is $2\varepsilon + U$, the additional positive energy U representing the intra-atomic Coulomb repulsion between the two localized electrons. (The exclusion principle prevents more than two electrons from occupying the level.)

The Hubbard model for a two-atom molecule consists of two such orbital levels, $|\mathbf{R}\rangle$ and $|\mathbf{R}'\rangle$, representing electrons localized at \mathbf{R} and \mathbf{R}' , respectively. For simplicity, one takes the two levels to be orthogonal:

$$\langle \mathbf{R} | \mathbf{R}' \rangle = 0. \quad (32.29)$$

We first consider the problem of two "protons" and one electron (i.e., H_2^+). If the one-electron Hamiltonian h were diagonal in $|\mathbf{R}\rangle$ and $|\mathbf{R}'\rangle$, the stationary levels would describe a hydrogen atom and a proton. We know, however, that if the protons are not too far apart, there will be a probability for the electron tunneling from one to the other, which leads to an ionized hydrogen molecule. We represent this amplitude for tunneling by an off-diagonal term in the one-electron Hamiltonian:

$$\langle \mathbf{R} | h | \mathbf{R}' \rangle = \langle \mathbf{R}' | h | \mathbf{R} \rangle = -t, \quad (32.30)$$

where we may choose the phases of $|\mathbf{R}\rangle$ and $|\mathbf{R}'\rangle$ to make the number t real and positive. This, in conjunction with the diagonal terms

$$\langle \mathbf{R} | h | \mathbf{R} \rangle = \langle \mathbf{R}' | h | \mathbf{R}' \rangle = \varepsilon, \quad (32.31)$$

defines the one-electron problem.

(a) Show that the one-electron stationary levels are

$$\frac{1}{\sqrt{2}} (|\mathbf{R}\rangle \mp |\mathbf{R}'\rangle) \quad (32.32)$$

with corresponding eigenvalues

$$\varepsilon \pm t. \quad (32.33)$$

As a first approach to the two-electron problem (the hydrogen molecule) we make the independent electron approximation for the singlet (spatially symmetric) ground state, putting both electrons into the one-electron level of lowest energy, to get a total energy of $2(\varepsilon - t)$. This ignores entirely the interaction energy U arising when two electrons are found on the same proton. The crudest way to improve upon the estimate $2(\varepsilon - t)$ is to add the energy U , multiplied by the probability of actually finding two electrons on the same proton, when the molecule is in the ground state of the independent electron approximation.

(b) Show that this probability is $\frac{1}{2}$, so that the improved independent electron estimate of the ground-state energy is

$$E_{sc} = 2(\varepsilon - t) + \frac{1}{2}U. \quad (32.34)$$

(This result is just the Hartree (or self-consistent field) approximation, applied to the Hubbard model. See Chapters 11 and 17.)

The full set of singlet (spatially symmetric) states of the two-electron problem are:

$$\begin{aligned} \Phi_0 &= \frac{1}{\sqrt{2}} (|\mathbf{R}\rangle|\mathbf{R}'\rangle + |\mathbf{R}'\rangle|\mathbf{R}\rangle), \\ \Phi_1 &= |\mathbf{R}\rangle|\mathbf{R}\rangle, \quad \Phi_2 = |\mathbf{R}'\rangle|\mathbf{R}'\rangle, \end{aligned} \quad (32.35)$$

where $|\mathbf{R}\rangle|\mathbf{R}'\rangle$ has electron 1 on the ion at \mathbf{R} , and electron 2 on the ion at \mathbf{R}' , etc.

(c) Show that the approximate ground state wave function in the independent electron approximation can be written in terms of the states (32.35) as

$$\Phi_{ie} = \frac{1}{\sqrt{2}} \Phi_0 + \frac{1}{2} (\Phi_1 + \Phi_2) \quad (32.36)$$

The matrix elements of the full two-electron Hamiltonian,

$$H = h_1 + h_2 + V_{12}, \quad (32.37)$$

in the space of singlet states are $H_{ij} = (\Phi_i, H\Phi_j)$, where

$$\begin{pmatrix} H_{00} & H_{01} & H_{02} \\ H_{10} & H_{11} & H_{12} \\ H_{20} & H_{21} & H_{22} \end{pmatrix} = \begin{pmatrix} 2\varepsilon & -\sqrt{2}t & -\sqrt{2}t \\ -\sqrt{2}t & 2\varepsilon + U & 0 \\ -\sqrt{2}t & 0 & 2\varepsilon + U \end{pmatrix} \quad (32.38)$$

Note that the diagonal elements in the states Φ_1 and Φ_2 that place two electrons on the same proton contain the extra Coulomb repulsion U ; the Coulomb repulsion is not present in the diagonal element in the state Φ_0 , since in Φ_0 the electrons are on different protons. This appearance of U is the only effect of the electron-electron interaction V_{12} . Note also that the one-electron tunneling amplitude t connects only states in which a single electron has been moved from one proton to the other (it would take a further two-body interaction to give a nonvanishing matrix element between states in which the positions of two electrons are changed). Convince yourself that the factor of $\sqrt{2}$ in (32.38) is correct.

The Heitler-London approximation to the singlet ground state is just Φ_0 , and therefore the Heitler-London estimate of the ground-state energy is just H_{00} , so

$$E_{HL} = 2\varepsilon. \quad (32.39)$$

(d) Show that the exact ground-state energy of the Hamiltonian (32.38) is

$$E = 2\varepsilon + \frac{1}{2}U - \sqrt{4t^2 + \frac{1}{4}U^2}. \quad (32.40)$$

Plot this energy, the independent electron approximation (32.34) to the ground-state energy, and the Heitler-London approximation to the ground-state energy as functions of U (for fixed ε and t). Comment on the behavior for large and small U/t and why it is physically reasonable. How do these three energies compare when $U = 2t$?

(e) Show that the exact ground state of the Hamiltonian (32.38) is (to within a normalization constant)

$$\Phi = \frac{1}{\sqrt{2}} \Phi_0 + \left(\sqrt{1 + \left(\frac{U}{4t}\right)^2} - \frac{U}{4t} \right) \frac{1}{2} (\Phi_1 + \Phi_2) \quad (32.41)$$

What is the probability in this state of finding two electrons on the same ion? Plot your answer as a function of U (for fixed ε and t) and comment on its behavior for small and large U/t .