

4.8 The two atoms containing molecule

The questions of the last section can not be answered generally even for the perfect periodic solid; this is e.g. exactly the focus of the actual solid state scientific effort for HTSC. Magnetic properties which are directly coupled to the Coulomb interaction between the electrons are not understood until now, but they are most probably the reason for the unexpected high transition temperatures in these superconductors.

To get a feeling for these problems and the strong coupling between magnetic properties and the Coulomb interaction between electrons, we will study the Hamiltonian of a two atomic molecule. Since this can again not be done exactly, we will apply a very effective and often used method to calculate an approximation.

The Ritz minimization method

Each wave function ψ which is not the ground state of the quantum mechanical system has a higher energy as the ground state ψ_0 , since

$$\psi = \sum_i a_i \Phi_i \quad 1 = \sum_i |a_i|^2 \quad (4.59)$$

and at least one a_i exists with $a_i > 0$. Therefore we get

$$\psi^* H \psi = \psi^* \sum_i a_i \Phi_i = \sum_i |a_i|^2 E_i > E_0 \quad (4.60)$$

We can get an upper limit for the ground state energy and an approximation for the ground state of a Hamiltonian when choosing a wave function $\psi(\lambda_i)$ with variational parameter λ_i and minimize the expectation value:

$$E_{approx} = \min_{\lambda_i} \psi^*(\lambda_i) H \psi(\lambda_i) \quad (4.61)$$

This method is often used in quantum mechanics. The results are becoming better when we chose a good (adequate) test function for the wave function.

HINT: This method can even be used to calculate the first excited state, minimizing the test function under the restriction that it has to be orthonormal to the ground state wave function.

The Hamiltonian of the two atoms containing molecule with two electrons

The Hamiltonian consists the kinetic and potential (Coulomb-) energy of both electrons

$$H\psi = -\frac{\hbar^2}{2m} (\Delta_1^2 + \Delta_2^2) \psi + V(r_1, r_2)\psi = E\psi \quad (4.62)$$

Neglecting the Coulomb force between electrons

$$\frac{e^2}{|r_1 - r_2|} \quad (4.63)$$

the Hamiltonian is written as

$$H\psi = (h_1 + h_2) \psi(r_1, r_2) = E\psi(r_1, r_2) \quad (4.64)$$

with

$$h_i = -\frac{\hbar^2}{2m} \Delta_i^2 - \frac{e^2}{|r_i - R_1|} - \frac{e^2}{|r_i - R_2|} \quad (4.65)$$

The charge of the atom core is chosen to be $1e$ (H_2 -molecule); a factor $1/4\pi\epsilon_0$ has been neglected.

Although the Hamiltonian in the equations (4.62)-(4.65) only needs explicitly the position of the electrons but not the spin, we have to take it into account for the complete wave function:

- The complete wave function has to be antisymmetric.
- No two electrons have the same quantum numbers.
- Since two electrons even with identical wave functions can differ in the spin, we have to take the spin into account for the solution of the Hamiltonian.