Quantum Theory of Condensed Matter I

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Sheet 4

1. Hydrogen molecule

Let us consider once again the one dimensional hydrogen molecule introduced in the Sheet 1. Yet we concentrate here on the electron-electron interaction *i.e.* we consider now the full (1D) hydrogen molecule.

1. Write the Hamiltonian for the hydrogen molecule in second quantization considering as a single particle basis the first two molecular orbitals calculated at point 1.1 of the numerical tutorial. This time, though, consider the spin. Which means that your single particle minimal basis has dimension 4. Prove that due to the symmetry of the molecular orbitals only 4 of the matrix elements for the interaction Hamiltonian do not vanish, namely:

$$U_{ee} = \int \mathrm{d}x \int \mathrm{d}x' \, \psi_e^*(x)\psi_e^*(x') \, \frac{2}{|x-x'|+\delta} \, \psi_e(x)\psi_e(x')$$

$$U_{oo} = \int \mathrm{d}x \int \mathrm{d}x' \, \psi_o^*(x)\psi_o^*(x') \, \frac{2}{|x-x'|+\delta} \, \psi_o(x)\psi_o(x')$$

$$U_{oe} = \int \mathrm{d}x \int \mathrm{d}x' \, \psi_o^*(x)\psi_e^*(x') \, \frac{2}{|x-x'|+\delta} \, \psi_o(x)\psi_e(x')$$

$$J = \int \mathrm{d}x \int \mathrm{d}x' \, \psi_o^*(x)\psi_e^*(x') \, \frac{2}{|x-x'|+\delta} \, \psi_e(x)\psi_o(x')$$

where the indices e and o stand for *even* and *odd* respectively, and label the first two molecular orbitals according to their spatial symmetry.

Consequently prove that the interaction part of the Hamiltonian reads:

$$\hat{H}_{int} = \; U_{ee} \, c_{e\uparrow}^\dagger c_{e\downarrow}^\dagger c_{e\downarrow} c_{e\uparrow} + U_{oo} \, c_{o\uparrow}^\dagger c_{o\downarrow}^\dagger c_{o\downarrow} c_{o\uparrow} + U_{eo} \sum_{\sigma\sigma'} c_{e\sigma}^\dagger c_{o\sigma'}^\dagger c_{o\sigma'} c_{e\sigma}$$

$$+ \, J \left[\sum_{\sigma\sigma'} c_{e\sigma}^\dagger c_{o\sigma'}^\dagger c_{e\sigma'} c_{o\sigma} + c_{e\uparrow}^\dagger c_{e\downarrow}^\dagger c_{o\downarrow} c_{o\uparrow} + c_{o\uparrow}^\dagger c_{o\downarrow}^\dagger c_{e\downarrow} c_{e\uparrow} \right].$$

(3 Points)

2. Prove that the 2-particle Hilbert space has dimension 6 and is spanned (for example) by the vectors:

$$|e\uparrow, e\downarrow\rangle, \quad |o\uparrow, o\downarrow\rangle, \quad |e\uparrow, o\downarrow\rangle, \quad |e\downarrow, o\uparrow\rangle, \quad |e\uparrow, o\uparrow\rangle, \quad |e\downarrow, o\downarrow\rangle.$$

Hint: Remember that a vector is well defined in the occupation representation only when an *order* is defined in the single particle basis!

(2 Points)

3. Calculate the matrix elements of the Hamiltonian written at points 1.1 and 1.2 with respect to the basis set of point 1.3. Prove that the eigenenergies are:

$$E_e + E_o + U_{eo} - J \qquad \text{three times degenerate}$$

$$E_e + E_o + \frac{U_{ee} + U_{oo}}{2} + \sqrt{\left(E_e - E_0 + \frac{U_{ee} - U_{oo}}{2}\right)^2 + J^2}$$

$$E_e + E_o + \frac{U_{ee} + U_{oo}}{2} - \sqrt{\left(E_e - E_0 + \frac{U_{ee} - U_{oo}}{2}\right)^2 + J^2}$$

$$E_e + E_o + U_{eo} + J$$

Associate to each of the eigenvalue the correspondent electronic state of the molecule (singlet or triplet).

Hint: Remember that the Hamiltonian that we are dealing with conserves the z component of the total spin on the system. This means that you can separate from the beginning subspaces that have $S^z_{tot} = 0, 1, -1$.

(3 Points)

4. Calculate and plot the eigenvalues of the hydrogen molecule in the Born-Oppenheimer approximation as a function of the interatomic distance D. Which is the electronic state of the stable molecule?

(3 Points)

Frohes Schaffen!