University of Regensburg Summer Semester 2008

Quantum Theory of Condensed Matter

Prof. Milena Grifoni Room H33
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Sheet 1

1. Rules of the game

Nothing else than "hands-on" approach helps to fix ideas, we will give than a lot of importance to the written exercises proposed on a weekly basis. In particular:

1. An exercise sheet is given at every Wednesday lecture. **Clearly written** solutions of the exercise sheets should be handed in by Tuesday of the following week at 12:00 in the post box of the course located in "*Treppenhaus 1. Etage* (*Bibliothek Physik*)". The exercise solutions will be then discussed during Wednesday exercise class.
2. One week of April and one of June will be dedicated to the computational laboratory. These particular exercise sheets will consist of a task to be solved with a computer simulation. You will be asked to develop a simple code that allows you to calculate and visualize some of the results obtained in the course. Linux CIP pool will be available for coding and running the simulations. Group sizes of 2-3 people are encouraged. Any program language can be used for the calculation but assistance can be ensured only for MATLAB®.

PART -A-

2. Hydrogen molecule (discretize the Schrödinger equation)

Let us consider a 1D model of a hydrogen molecule. In particular we study only one electron in the system thus restricting ourselves to the hydrogen molecule ion.

1. Write the Hamiltonian for the system in Born-Oppenheimer approximation. Prove that, if all lengths are written in units of the Bohr radius a_0, and all energies in units of the modulus of the eigenenergy $|E_1|$ of the $1s$ orbital of hydrogen, the Schrödinger equation reads:

$$\left(-\frac{d^2}{d\xi^2}-\frac{2}{|\xi+D/2|}-\frac{2}{|\xi-D/2|}+\frac{2}{D}\right)\psi_n(\xi)=E_n(D)\psi_n(\xi)$$

   where D is the (renormalized) distance between the protons and $V_0(\xi)=\frac{2}{|\xi|}$ is the Coulomb interaction.

   Hint: The Bohr radius a_0 and the hydrogen eigenenergy E_1 in terms of fundamental constants read, respectively:

$$a_0=\frac{4\pi\varepsilon_0\hbar^2}{me^2}\approx 0.053\,\text{nm}$$
$$E_1=\frac{me^4}{2(4\pi\varepsilon_0)^2\hbar^2}\approx -13.6\,e\text{V}$$

   where e and m are the charge and the rest mass of the electron and ε_0 the vacuum dielectric constant.

Now you will discretize the equation stated at point 1 and thus transform the eigenvalue problem to make it suitable for a numerical calculation.

2. Replace the continuous space variable ξ with the discrete set of numbers ξ_i with $i=1,\ldots,N$. The wave-function is thus replaced by a vector: which one?

3. Work out the discrete version of the derivative. Eventually represent it as a matrix acting on the discrete wave function calculated in the previous point.

4. Also the second derivative is an operator which acts on the wave function. Find out which is its matrix representation in the discrete space introduced in the previous points.

5. Complete the discretization process and write the full eigenvalue problem as an algebraic equation:

$$\mathbf{H}\psi_{\mathbf{n}} = \mathbf{E}_{\mathbf{n}}\psi_{\mathbf{n}}$$

(Hint: Remember that the potential operator acts locally $(V\psi)(\xi) = V(\xi)\psi(\xi)$.)

PART -B-

3. Hydrogen molecule ion (molecular orbitals)

Let's analyze the numerical solution of the eigenvalue problem stated in the Exercise 2.

1. Calculate and plot the eigenstates corresponding to the lowest eigenvalues (*i.e.* the low energy molecular orbitals.). A truncated version of the Coulomb potential (still in "atomic units"):

$$V_\delta(\xi) = \frac{2}{|\xi| + \delta},$$

is useful to avoid divergences. The convergence of the results in the limit $\delta \to 0$ can be eventually checked in the end of the calculation.

2. Make a plot of the first two eigenvalues of the Born-Oppenheimer Hamiltonian as a function of the interatomic distance D. Is the molecule stable? Which is the spatial symmetry of the ground state (even or odd)?

3. In the discretization process you have to introduce (at least) one parameter: the distance a between neighbours point on the space grid. It turns out that for the problem at hand $a \ll \delta$ is a necessary condition to get reasonable results. Can you say why?

4. Hydrogen molecule ion (atomic orbitals)

We now consider the same problem of point 1. starting though from the atomic orbitals.

1. Write the hamiltonian for a 1D hydrogen atom in "atomic units" and discretize it. Diagonalize numerically.

2. Use the ground state calculated at the previous point and assume that the single particle Hilbert space of the hydrogen molecule is spanned by the ground states of the hydrogen atom centered on the first and second hydrogen. Eventually write the equation of point 2.1 in this atomic orbital basis. Calculate now numerically the matrix elements of the Hamiltonian and the overlap matrix S.

3. Solve the eigenvalue problem stated at the previous point first in the approximation $S_{ij} = \delta_{ij}$. Plot the eigenvalues as a function of the interatomic distance D. Check that in the large D limit the 2 eigenenergies coincide and correspond to the energy of the isolated hydrogen atom. Compare the results also with the ones of point 3.2.

4. Repeat the previous point releasing the approximation done on the overlap matrix S. Check that in this case the correspondance to the solution obtained using molecular orbitals is closer. Still there are some discrepancies for small D. Can you say why?

Frohes Schaffen!