

Quantum Theory of Condensed Matter

Prof. Milena Grifoni
Dr. Andrea Donarini

Room H33
Wednesdays at 13:15

Sheet 9

1. Hydrogen molecule ion (molecular orbitals)

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 quantities reads, respectively:

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{me^2} \approx 0.053 \text{ nm}$$

$$E_1 = \frac{me^4}{2(4\pi\epsilon_0)^2\hbar^2} \approx -13.6 \text{ eV}$$

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

2. Numerical solution of the equation stated at point 1. For the numerical calculation discretize the space $\xi \rightarrow \xi_n$ with $n = 1, \dots, N$. Now the wave-function is a vector since $\psi(\xi) \rightarrow \psi(\xi_n)$. The discrete version of the derivative now reads $\psi'(\xi_n) = (\psi(\xi_{n+1}) - \psi(\xi_{n-1})) / (\xi_{n+1} - \xi_{n-1})$. Work out analogously the second derivative and, finally, remember that the potential operator acts locally $(V\psi)(\xi) = V(\xi)\psi(\xi)$. Put all together and you have transformed the single particle Schrödinger equation into an algebraic equation that can be solved numerically. 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 $\delta \rightarrow 0$ can be eventually checked in the end of the calculation.

3. 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)?
4. 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?

Hint: Start considering the kinetic part of the electronic Hamiltonian. It is basically a tight binding Hamiltonian for a translationally invariant system. The eigenstates can be labelled using momentum. Though is the spectrum quadratic in the momentum? How can you improve the resemblance to a quadratic spectrum?

2. 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 1.1 in this atomic orbital basis. Calculate now numerically the matrix elements of the Hamiltonian and the overlap matrix S .
3. Solve the problem stated at point 2.1. 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 1.3.
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?

3. Hydrogen molecule

Eventually we insert the second electron and 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 (spin degenerate) molecular orbitals calculated at point 1.2. Prove that due to the symmetry of the molecular orbitals only 4 of the matrix element for the interaction Hamiltonian do not vanish, namely:

$$\begin{aligned}
 U_{ee} &= \int dx \int dx' \psi_e^*(x) \psi_e^*(x') \frac{2}{|x-x'|+\delta} \psi_e(x) \psi_e(x') \\
 U_{oo} &= \int dx \int dx' \psi_o^*(x) \psi_o^*(x') \frac{2}{|x-x'|+\delta} \psi_o(x) \psi_o(x') \\
 U_{oe} &= \int dx \int dx' \psi_o^*(x) \psi_e^*(x') \frac{2}{|x-x'|+\delta} \psi_o(x) \psi_e(x') \\
 J &= \int dx \int dx' \psi_o^*(x) \psi_e^*(x') \frac{2}{|x-x'|+\delta} \psi_e(x) \psi_o(x')
 \end{aligned}$$

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:

$$\begin{aligned}
 \hat{H}_{int} &= U_{ee} c_{e\uparrow}^\dagger c_{e\downarrow}^\dagger c_{e\downarrow} c_{e\uparrow} + U_{oo} c_{o\uparrow}^\dagger c_{o\downarrow}^\dagger c_{o\downarrow} c_{o\uparrow} \\
 &+ U_{eo} \sum_{\sigma\sigma'} c_{e\sigma}^\dagger c_{o\sigma'}^\dagger c_{o\sigma'} c_{e\sigma} + J \sum_{\sigma\sigma'} c_{e\sigma}^\dagger c_{o\sigma'}^\dagger c_{e\sigma'} c_{o\sigma}.
 \end{aligned}$$

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!

3. Calculate the matrix elements of the Hamiltonian calculated at points 3.1 and 3.2 with respect to the basis set of point 3.3. Prove that the eigenenergies are:

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

$$2E_e + U_{ee}$$

$$2E_o + U_{oo}$$

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

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 $S_{tot}^z = 0, 1, -1$.

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?

Frohes Schaffen!

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clear all

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%
%       The Hydrogen molecule in 1D
%
%   numerical sheet 9 for the QTKM1 SS 07
%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%
%       Hydrogen molecule ion
%       (molecular orbitals)
%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

%all lengths are measured in units of the Bohr radius 0.053 nm
%all energies are measured in units of the 1s hydrogen energy level 13.6 eV;

dx = 0.02;      %discretization step
xmax = 4;      %upper limit of the space
d = 0.1;       %cure of the Coulomb divergence

Dvet = [0.1:0.1:4];      %vector of the interatomic distances
xvet = -xmax:dx:xmax;    %vector of positions

%Construction of the kinetic part of the Hamiltonian
%(independent of the interatomic distance D)

T = 1/dx^2*(...
    diag(2*ones(1,length(xvet)))...
    -diag(ones(1,length(xvet)-1),1)...
    -diag(ones(1,length(xvet)-1),-1));
%Implementation of periodic boundary conditions
T(1,length(xvet)) = -1;
T(length(xvet),1) = -1;

for i = 1:length(Dvet) %loop for the different distances D
    tic
    D = Dvet(i);

%definition of the molecular Coulomb potential
%notice that the 2 here is just due to the energy renormalization

V = -2*diag(1./(abs(xvet - D/2)+d))-2*diag(1./(abs(xvet + D/2)+d));

%construction of the electronic Hamiltonian in Born-Oppenheimer
%approximation
H_0 = T + V;

%diagonalization of the B-O Hamiltonian. En is the matrix of the
%eigenvalues and Psi is the unitary matrix that diagonalize H_0.
%In other terms it is the matrix build up with all the eigenvectors.
[Psi,En]=eig(H_0);

%vector of the eigenenergies
Energie = diag(En);
```

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%extraction of the lowest 2 eigenenergies. The last term is the
%proton-proton repulsion.

LowEn(:,i) = Energie(1:4) + 2/(D + d);
LowPsi(:, :, i) = Psi(:, 1:4);
Pot(:, i) = diag(V);
%count down
countdown = length(Dvet) - i
toc
end
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%                               Graphics                               %
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

figure(1)

subplot(2,2,1)
plot(Dvet, LowEn, 'Linewidth', 2)
title('Eigenenergies', 'FontSize', 15)
xlabel('\xi', 'FontSize', 15)
ylabel('E', 'FontSize', 15)

subplot(2,2,2)
N = 20;
Max = 1.1 * max(max(squeeze(LowPsi(:, 1, N))), max(squeeze(LowPsi(:, 2, N))));
vet = -Max : 0.01 : Max;
plot(Dvet(N) / 2 * ones(length(vet)), vet, 'k--')
hold on
plot(-Dvet(N) / 2 * ones(length(vet)), vet, 'k--')
plot(xvet, squeeze(LowPsi(:, 1:2, N)), 'Linewidth', 2)
title('Eigenstates', 'FontSize', 15)
xlabel('\xi', 'FontSize', 15)
ylabel('\psi(\xi)', 'FontSize', 15)
axis tight
hold off

subplot(2,2,3)
surf(xvet, Dvet, squeeze(LowPsi(:, 1, :)).^2)
view([0 90])
shading interp
axis tight
title('Even state', 'FontSize', 15)
xlabel('\xi', 'FontSize', 15)
ylabel('D', 'FontSize', 15)

subplot(2,2,4)
surf(xvet, Dvet, squeeze(LowPsi(:, 2, :)).^2)
view([0 90])
shading interp
axis tight
title('Odd state', 'FontSize', 15)
xlabel('\xi', 'FontSize', 15)
ylabel('D', 'FontSize', 15)

save Hyd_ion_MO.mat LowEn LowPsi Pot
```

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clear all

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%
%   numerical sheet 9 for the QTKM1 SS 07
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dx = 0.02;      %discretization step
xmax = 4;      %upper limit of the space
d = 0.1;       %cure of the Coulomb divergence

Dvet = [0.1:0.1:4];      %vector of the interatomic distances
xvet = -xmax:dx:xmax;   %vector of positions

%Construction of the kinetic part of the Hamiltonian
%(independent of the interatomic distance D)

T = 1/dx^2*(...
    diag(2*ones(1,length(xvet)))...
    -diag(ones(1,length(xvet)-1),1)...
    -diag(ones(1,length(xvet)-1),-1));
%Implementation of periodic boundary conditions
T(1,length(xvet)) = -1;
T(length(xvet),1) = -1;

for i = 1:length(Dvet)
    tic
    D = Dvet(i);
    %notice that the 2 here is just due to the energy renormalization
    %we are defining the 2 potentials for the 2 protons separately
    V1 = -2*diag(1./(abs(xvet + D/2)+d));
    V2 = -2*diag(1./(abs(xvet - D/2)+d));

    %hamiltonian with only the first proton
    H_0 = T + V1;

    %eigenvalues and eigenstates
    [Psi,En]=eig(H_0);

    %we take the ground state
    Psi1 = Psi(:,1);
    %construction of the ground state for the second proton
    %using the symmetry of the problem
    Psi2 = flipud(Psi1);

    %now the total Hamiltonian
```

H = T + V1 + V2;

%this are the matrix elements of the Hamiltonian
H_t(1,1) = Psi1'*H*Psi1;
H_t(1,2) = Psi1'*H*Psi2;
H_t(2,1) = Psi2'*H*Psi1;
H_t(2,2) = Psi2'*H*Psi2;

%This is the overlap matrix S
S(1,1) = Psi1'*Psi1;
S(1,2) = Psi1'*Psi2;
S(2,1) = Psi2'*Psi1;
S(2,2) = Psi2'*Psi2;

%solution of the problem without overlap
[Psi_t,En_t] = eig(H_t);

%spectrum and eigenstates without overlap
LowEn_t(:,i) = sort(diag(En_t)) + 2/(D+d);
Psi_t_1(:,i)= 1/sqrt(2)*(Psi1 + Psi2);
Psi_t_2(:,i)= 1/sqrt(2)*(Psi1 - Psi2);

%solution of the problem with overlap
[Psi_ts,En_ts] = eig(inv(S)*H_t);

%spectrum and eigenstates with overlap
LowEn_ts(:,i) = sort(diag(En_ts)) + 2/(D+d);
Psi_ts_1(:,i)= Psi_ts(1,1)*Psi1 + Psi_ts(2,1)*Psi2;
Psi_ts_2(:,i)= Psi_ts(1,2)*Psi1 + Psi_ts(2,2)*Psi2;

%countdown
length(Dvet) - i
toc
end

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Graphics %
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

figure(1)

load Hyd_ion_MO.mat
subplot(1,2,1)
plot(Dvet, LowEn(1:2,:), 'Linewidth',2)
hold on
plot(Dvet, LowEn_t, 'r')
hold on
plot(Dvet, LowEn_ts, 'k')
title('Eigenenergies', 'FontSize',15)
xlabel('D', 'FontSize',15)
ylabel('E', 'FontSize',15)

N=20
subplot(1,2,2)
plot(xvet, Psi_t_1(:,N), 'Linewidth',2)
hold on
plot(xvet, Psi_t_2(:,N), 'Linewidth',2)
plot(xvet, Psi_ts_1(:,N), 'g--', 'Linewidth',2)
plot(xvet, Psi_ts_2(:,N), 'g--', 'Linewidth',2)

```
title('Eigenstates','FontSize',15)
xlabel('\xi','FontSize',15)
ylabel('\psi(\xi)','FontSize',15)
axis tight
hold off

figure(2)
subplot(2,2,1)
surf(xvet,Dvet,squeeze(LowPsi(:,1,:)).^2')
view([0 90])
shading interp
axis tight
title('Even state MO','FontSize',15')
xlabel('\xi','FontSize',15')
ylabel('D','FontSize',15')

subplot(2,2,2)
surf(xvet,Dvet,squeeze(LowPsi(:,2,:)).^2')
view([0 90])
shading interp
axis tight
title('Odd state MO','FontSize',15')
xlabel('\xi/a_0','FontSize',15')
ylabel('D','FontSize',15')

subplot(2,2,3)
surf(xvet,Dvet,Psi_t_1.^2')
view([0 90])
shading interp
axis tight
title('Even state AO','FontSize',15')
xlabel('\xi','FontSize',15')
ylabel('D','FontSize',15')

subplot(2,2,4)
surf(xvet,Dvet,Psi_t_2.^2')
view([0 90])
shading interp
axis tight
title('Odd state AO','FontSize',15')
xlabel('\xi','FontSize',15')
ylabel('D','FontSize',15')
```



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clear all

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%
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%
%   numerical sheet for the QTKM1 SS 07
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%       Hydrogen molecule
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%all lengths are measured in units of the Bohr radius 0.053 nm
%all energies are measured in units of the 1s hydrogen energy level 13.6 eV;

dx = 0.02;      %discretization step
xmax = 4;      %upper limit of the space
d = 0.1;       %cure of the Coulomb divergence

Dvet = [0.1:0.1:4];      %vector of the interatomic distances
xvet = -xmax:dx:xmax;   %vector of positions

%Construction of the kinetic part of the Hamiltonian
%(independent of the interatomic distance D)

T = 1/dx^2*(...
    diag(2*ones(1,length(xvet)))...
    -diag(ones(1,length(xvet)-1),1)...
    -diag(ones(1,length(xvet)-1),-1));
%Implementation of periodic boundary conditions
T(1,length(xvet)) = -1;
T(length(xvet),1) = -1;

%Construction of the Coulomb interaction matrix
for j=1:length(xvet)
    Coul(j,:) = 2./(abs(xvet - xvet(j))+d);
end

%loop for different interatomic distances D
for i = 1:length(Dvet)
    tic
    D = Dvet(i);
    %definition of the molecular Coulomb potential
    %notice that the 2 here is just due to the energy renormalization

    V = -2*diag(1./(abs(xvet - D/2)+d))-2*diag(1./(abs(xvet + D/2)+d));

    %construction of the electronic Hamiltonian in Born-Oppenheimer
    %approximation
    H_0 = T + V;

    %diagonalization of the B-O Hamiltonian. En is the matrix of the
    %eigenvalues and Psi is the unitary matrix that diagonalize H_0.
```

%In other terms it is the matrix build up with all the eigenvectors.

[Psi,En]=eig(H_0);

%vector of the eigenenergies

Energie = diag(En);

%extraction of the single particle energies

E_e = Energie(1);

E_o = Energie(2);

%extraction of the single particle eigenstates

Psi_e = Psi(:,1);

Psi_o = Psi(:,2);

%calculation of the interaction integrals

U_ee = Psi_e'.^2*Coul*Psi_e.^2;

U_oo = Psi_o'.^2*Coul*Psi_o.^2;

U_oe = Psi_o'.^2*Coul*Psi_e.^2;

U_eo = Psi_e'.^2*Coul*Psi_o.^2;

J = (Psi_e'.*Psi_o')*Coul*(Psi_e.*Psi_o);

%calculation of the interacting electron eigenenergies

Tr(i) = E_e + E_o + U_eo - J;

Si_e(i) = 2*E_e + U_ee;

Si_o(i) = 2*E_o + U_oo;

Si_eo(i) = E_e + E_o + U_eo + J;

%ground state of the molecule

Ground(i) = min([Tr(i),Si_e(i),Si_o(i),Si_eo(i)]) + 2/(D + d);

toc

end

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% Graphics %
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

figure(1)

plot(Dvet,Tr + 2./(Dvet + d),'r')

hold on

plot(Dvet,Si_e + 2./(Dvet + d),'g')

plot(Dvet,Si_o + 2./(Dvet + d),'b')

plot(Dvet,Si_eo + 2./(Dvet + d),'k')

title('Eigenenergies','FontSize',15)

xlabel('\xi','FontSize',15)

ylabel('E','FontSize',15)