

Esercitazione °3: molecules H_2^+ and H_2

Exercise I : Molecular Ion H_2^+

We consider the molecular ion H_2^+ . We will limit ourself to a finite Hilbert space generated by the $|1s\rangle$ states of the two H atoms. We call $|A\rangle$ the state of the A atom and $|B\rangle$ the state of the B atom. The states are normalised and we neglect the overlap between states of different atoms, namely we suppose that $\langle A|B\rangle = 0$. In this restricted space, the matrix elements of the Hamiltonian are:

$$\langle A|H|A\rangle = \langle B|H|B\rangle = -E_0(d) \quad (1)$$

$$\langle A|H|B\rangle = \langle B|H|A\rangle = -t(d), \quad (2)$$

where d is the H_A-H_B interatomic distance.

1. Show that E_0 and t are real.
2. What is the sign of t
3. Describe the behaviour of t for $d \rightarrow +\infty$
4. Compute the eigenstates and eigenvalues of H
5. Represent qualitatively the ground state and excited state wave-functions on the AB axis

Exercise II : H_2 molecule

We consider the 2-electron Hamiltonian of the molecule $H = H^{1e,1} + H^{1e,2} + H^{2e}$, where

$$H^{1e,1} = -E_0 [|A\rangle_1 \langle A| + |B\rangle_1 \langle B|] - t [|A\rangle_1 \langle B| + |B\rangle_1 \langle A|]$$

$$H^{1e,2} = -E_0 [|A\rangle_2 \langle A| + |B\rangle_2 \langle B|] - t [|A\rangle_2 \langle B| + |B\rangle_2 \langle A|]$$

$$H^{2e} = U [|A\rangle_1 \langle A| |A\rangle_2 \langle A| + |B\rangle_1 \langle B| |B\rangle_2 \langle B|].$$

Here E_0 , t $|A\rangle$ and $|B\rangle$ have the same meaning as in the preceding exercise, $U > 0$ is the energy (Coulomb repulsion) present when the two electrons are placed on the same atom, and the indexes 1 and 2 refer to the Hilbert spaces of electrons 1 and 2.

1. Exact solution

- (a) Does the Hamiltonian commute with the total spin operator \mathbf{S} ?

- (b) Give the dimension of the 2-electron Hilbert space
- (c) Give all the eigenvalues and the eigenvectors of H (for the 2-electron case) when we neglect the e-e interaction. To this goal determine the Slater determinants that diagonalise H with $U = 0$.
- (d) For the $U = 0$, construct the combinations of Slater determinants that are common eigenstates of the operators \mathbf{S}^2 , S_z and H .
- (e) Let's consider the operator P_{AB} that exchanges the site A with the site B , namely $P_{AB}|A\rangle = |B\rangle$ and $P_{AB}|B\rangle = |A\rangle$. How is the operator written in the 2-electron case (consider the analogy with the operator \mathbf{S})? What are the possible eigenvalues of this operator? Does P_{AB} commute with H (consider both the cases with $U = 0$ and $U \neq 0$)? Does P_{AB} commute with \mathbf{S}^2 and S_z ? Can we choose eigenstates of H that are also eigenstates of P_{AB} (consider both the cases with $U = 0$ and $U \neq 0$)? Show that the eigenstates obtained at point (d) satisfy this condition.
- (f) In the case $U \neq 0$, write the matrix H using, as basis, the states found at point (d). Do the symmetries discussed at the previous points allow to set to zero (without explicit calculations) some element of such a matrix?
- (g) Diagonalise the matrix. Plot the ground-state and excited-state eigenenergies as a function of U/t . Discuss the results in the two limits $U/t \rightarrow \infty$ and $U/t \rightarrow 0$.

2. Restricted Hartree-Fock

In the restricted HF we impose that the spin-up wavefunctions in the Slater determinant are equal to the spin-down. The resulting determinant is a singlet state with total spin equal to zero. Thus we preserve in the approximation the spin symmetry of H . In our case we can pose $|D\rangle = \cos\theta|A\rangle + \sin\theta|B\rangle$ and the most general Slater determinant can be written as:

$$|\Psi\rangle = \frac{1}{\sqrt{2}} \begin{vmatrix} |D\rangle_1 | \uparrow \rangle_1 & |D\rangle_1 | \downarrow \rangle_1 \\ |D\rangle_2 | \uparrow \rangle_2 & |D\rangle_2 | \downarrow \rangle_2 \end{vmatrix}$$

- (a) Show that $|\Psi\rangle$ is an eigenstate of \mathbf{S} with zero eigenvalue.
- (b) Determine the restricted HF ground state energy. Compare it to the exact result, in particular, in the two limits $U/t \rightarrow \infty$ and $U/t \rightarrow 0$.

3. Unrestricted Hartree-Fock

In the unrestricted HF we allow the spin-up wavefunctions to be different from the spin-down ones. In this case we break the spin-symmetry of H . The most general Slater determinant is now:

$$|\Psi\rangle = \frac{1}{\sqrt{2}} \begin{vmatrix} |D\rangle_1 | \uparrow \rangle_1 & |D'\rangle_1 | \downarrow \rangle_1 \\ |D\rangle_2 | \uparrow \rangle_2 & |D'\rangle_2 | \downarrow \rangle_2 \end{vmatrix}$$

where $|D\rangle = \cos\theta|A\rangle + \sin\theta|B\rangle$ and $|D'\rangle = \sin\theta|A\rangle + \cos\theta|B\rangle$.

- (a) Is $|\Psi\rangle$, in general, an eigenstate of \mathbf{S}^2 and S_z ?
- (b) Find the unrestricted HF ground state by minimising the energy. In particular find the optimal value of $\sin 2\theta$ as a function of U/t .

- (c) Discuss the result in the limits $U/t \rightarrow \infty$ and $U/t \rightarrow 0$. Compare it to the restricted Hartree-Fock case.
- (d) For $U/t \rightarrow +\infty$, compute $\frac{E_{\text{triplet exact}} - E_{\text{UHF}}}{E_{\text{triplet exact}} - E_{S_0\text{exact}}}$, where $E_{\text{triplet exact}}$ is the energy of exact $S = 1$ state, $E_{S_0\text{exact}}$ the energy of the lowest exact $S = 0$ state and E_{UHF} is the unrestricted HF energy. Discuss the result.
4. By analogy with the standard e-e Hamiltonian, define and compute the E^{1e} , the Hartree, and Exchange energy for the restricted and unrestricted HF solutions. Plot and analyse the results as a function of the U/t (consider the two limits $U/t \rightarrow \infty$ and $U/t \rightarrow 0$). Comment the results.
5. For the exact solution ground-state compute the expectation value of the 1-electron and 2-electron Hamiltonian. Plot and analyse the results as a function of the U/t (consider the two limits $U/t \rightarrow \infty$ and $U/t \rightarrow 0$). Comment the results.
6. Define and compute the pair correlation function g . Compute it for the exact ground state and the for the restricted and unrestricted HF solutions as a function function of the U/t ratio. Comment the results.