

Frankfurt, 04.07.2022

Höhere Quantenmechanik
Summer term 2022

Exercise sheet 12

(Submission date: Until 11.07.2022 12:00)

Es werden mündliche Prüfungen zu zwei Terminen angeboten: Di 16. August und Di 30. August.

Anmeldung bis 31. Juli per eMail an C. Gros. Nach der Anmeldung erhalten Sie eine Bestätigung und später die Uhrzeit. Für die Anmeldung benötigen Sie zudem das entsprechende Anmeldeformular, wie es von der Webseite der Universität heruntergeladen werden kann. Dieses ist zur Prüfung mitzubringen. Ein teilweise schon ausgefüllte Formular finden Sie hier.

Exercise 1: variational method (basic principles) (6 Points)

We consider a generic Hamiltonian \mathcal{H} , with eigenvalues E_n and (normalized) eigenstates $|\phi_n\rangle$, labelled by the integer index n such that $E_0 < E_1 < E_2 < \dots$ (i.e., no degeneracy is present). Within a variational approach, one tries to approximate the ground state of \mathcal{H} by a certain trial wave function, denoted by $|\Psi_{var}\rangle$. The variational principle states that the variational energy, i.e. the expectation value of \mathcal{H} over the state $|\Psi_{var}\rangle$, is always larger than (or equal to) the exact ground state energy, i.e.

$$E_{var} = \frac{\langle \Psi_{var} | \mathcal{H} | \Psi_{var} \rangle}{\langle \Psi_{var} | \Psi_{var} \rangle} \geq E_0 \quad (1)$$

- (i) Prove the variational principle. (3 Points)

Hint: expand $|\Psi_{var}\rangle$ over the eigenstates of \mathcal{H} (and normalize it).

- (ii) The variational principle implies that the energy of any trial wave function $|\Psi_{var}\rangle$ will be an upper bound of the exact energy. Thus, in actual variational calculations, one tries to devise a clever variational state $|\Psi_{var}\rangle$ and tune its parameters to minimize E_{var} , in order to find the best approximation for the ground state energy. Assuming that $|\Psi_{var}\rangle$ is normalized, we can quantify the distance between $|\Psi_{var}\rangle$ and the exact ground state $|\phi_0\rangle$ by the quantity

$$\delta = 1 - |\langle \phi_0 | \Psi_{var} \rangle|^2 \geq 0$$

The distance δ vanishes only when $|\Psi_{var}\rangle$ is equal to the exact ground state.

Therefore, it is clear that small values of δ indicate that the trial wave function is close to the exact ground state. Show that

$$\delta < \frac{E_{var} - E_0}{E_1 - E_0}$$

This useful equation shows that, in order to have a good approximation of the ground state wave function (i.e. $\delta \ll 1$), it is sufficient that the variational error on the ground state energy is smaller than the gap to the first excited state, $(E_1 - E_0)$. (3 Points)

Exercise 2: variational method (application) (7 Points)

Consider a non-relativistic particle with mass m in one dimension ($x \in [-\infty, \infty]$), subjected to a potential

$$V(x) = -a \exp(-\alpha x^2)$$

with $a, \alpha \in \mathbb{R}$ and $a, \alpha > 0$. Using the variational method with the trial wave function

$$|\Psi_{var}\rangle = b \exp(-\beta x^2),$$

with $b, \beta \in \mathbb{R}$ and $\beta > 0$, show that there exists (at least) one bound state in the exact spectrum of the Hamiltonian.

Hints: sketch the behaviour of the variational energy as a function of β . Throughout the exercise, you may want to use the result for the Gaussian integral

$$\int_{-\infty}^{\infty} e^{-A(x+B)^2} dx = \sqrt{\frac{\pi}{A}} \quad (A > 0)$$

Bonus question (1 extra point): assuming that $|\Psi_{var}\rangle$ is a good approximation of the exact ground state, can you think of another trial wave function which could be used to target an excited state of the Hamiltonian?

Exercise 3: benzene (C_6H_6) (7 Points)

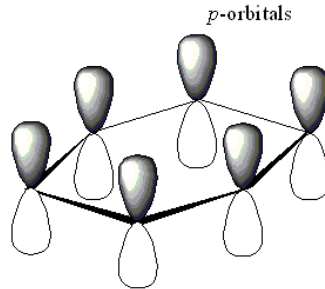


Figure 1: Benzene molecule with the p -orbitals of C atoms involved in the tight-binding model.

Benzene is an organic molecule containing six carbon atoms and six hydrogen atoms, arranged in an hexagonal shape. We want to consider a minimal *tight-binding model* for benzene, involving only the $2p$ -orbitals of the carbon atoms which are perpendicular to the plane of the molecule (see Fig. 1)¹. For simplicity, we can ignore the spin degree of freedom, which does not play a relevant role for this exercise. We can write the Hamiltonian of benzene as

$$\mathcal{H} = -t \sum_{n=0}^5 (c_n^\dagger c_{(n+1) \bmod 6} + c_{(n+1) \bmod 6}^\dagger c_n),$$

where c_n^\dagger and c_n respectively create and destroy an electron in the p -orbital of the n th carbon in the hexagonal ring, and t is a constant. The six carbon atoms are labelled by $n \in [0, 1, 2, 3, 4, 5]$. Note: we assume that the usual anticommutation relations for fermions hold, i.e. $\{c_n, c_m^\dagger\} = \delta_{n,m}$.

- (i) What physical processes are described by the terms forming the Hamiltonian? (1 Point)

¹the other $2p$ -orbitals and the $2s$ -orbital of each carbon atom form planar sp^2 orbitals.

- (ii) To find the eigenvalues of the Hamiltonian, we can perform a basis change, introducing the new fermionic operators d_k and d_k^\dagger for the molecular orbitals of benzene, such that

$$c_n = \frac{1}{\sqrt{6}} \sum_k e^{i\frac{2\pi}{6}kn} d_k$$

$$d_k = \frac{1}{\sqrt{6}} \sum_n e^{-i\frac{2\pi}{6}kn} c_n$$

with $k \in [0, 1, 2, 3, 4, 5]$. Use the transformation to rewrite the Hamiltonian in the diagonal form

$$\mathcal{H} = \sum_k E_k d_k^\dagger d_k,$$

where E_k are eigenenergies of benzene. (2 Points)

- (iii) How are the energy levels of the molecule? What value of k gives the lowest-energy orbital? How does the associated molecular orbital look like in real space? (2 Points)
- (iv) So far we have ignored the spin degree of freedom for simplicity. In reality, all the molecular levels that you have found can be filled by two electrons, one with spin \uparrow and one with spin \downarrow . In other words, the Hamiltonian is

$$\mathcal{H} = \sum_k \sum_{\sigma=\uparrow,\downarrow} E_k d_{k,\sigma}^\dagger d_{k,\sigma}.$$

Note: the energies E_k do not depend on the spin and are the ones that you found in the previous point. Knowing that the system contains 6 electrons and that $t \approx 2$ eV, give an estimate of the absorption spectrum of benzene. Is it a coloured substance? (2 Points)