Problem 1: Van der Waals interaction (Written)

Learning objective

Here you apply non-degenerate perturbation theory to calculate the van der Waals interaction between two hydrogen atoms. You will derive the radial dependency of this force for two atoms in the ground state. This application demonstrates that perturbation theory is an indispensable tool for quantum mechanics.

Consider two hydrogen atoms A and B with nuclei at $\mathbf{R}_A = \mathbf{0}$ and $\mathbf{R}_B = \mathbf{R}$ and large distance $|\mathbf{R}|$, so that the overlap of their charge distributions is negligible; furthermore, assume that their nuclei are fixed in space (Born-Oppenheimer approximation). Let H_i denote the Hamiltonian of a single hydrogen atom. The system can then be described by the Hamiltonian

$$H = H_A + H_B + H_{\text{int}}, \tag{1}$$

where H_{int} describes the Coulomb interaction of the electrons and the nuclei (protons), i.e.,

$$H_{\text{int}} = \frac{e^2}{|\mathbf{R}|} + \frac{e^2}{|\mathbf{R} + \mathbf{r}_B - \mathbf{r}_A|} - \frac{e^2}{|\mathbf{R} + \mathbf{r}_B|} - \frac{e^2}{|\mathbf{R} - \mathbf{r}_A|}, \tag{2}$$

with $\mathbf{r}_i$ ($i \in \{A, B\}$) the position of the electrons relative to their nucleus at $\mathbf{R}_i$. For large $|\mathbf{R}| \gg a_0$ (Bohr radius) one can expand H_{int} in powers of $1/|\mathbf{R}|$ (multipole expansion); since the atoms are neutral, the first contribution is the dipole-dipole interaction

$$H_{\text{int}} = \frac{1}{|\mathbf{R}|^3} \left[\mathbf{d}_A \cdot \mathbf{d}_B - \frac{3(\mathbf{d}_A \cdot \mathbf{R})(\mathbf{d}_B \cdot \mathbf{R})}{|\mathbf{R}|^2} \right] \tag{3}$$

with the dipole operators $\mathbf{d}_i \equiv e\,\mathbf{r}_i$.

In the following, we calculate the energy corrections due to this perturbation for the state $|g\rangle_A |g\rangle_B$ where both atoms are in their lowest energy eigenstates $|g\rangle_i$. To this end, we keep the distance $\mathbf{R}$ between the atoms fixed. Then, the energy correction $\Delta E(\mathbf{R})$ becomes parametrically dependent on the atom distance $\mathbf{R}$, which is interpreted as interaction between the atoms in the so called Born-Oppenheimer approximation.

a) Show that there is no contribution to $\Delta E(\mathbf{R})$ from first order perturbation theory.

To evaluate contributions in second order, we consider a simplified model where the dipole operator only couples to a *single* excited state $|e\rangle_i$ with principal quantum number $n = 2$, i.e., $\langle e|_i \mathbf{d}_i |g\rangle_i = d/\sqrt{3}\,\mathbf{e}_z$ where $\mathbf{e}_z$ denotes the unit vector in z-direction.

b) Show that the second order contribution to $\Delta E(\mathbf{R})$ is always negative and hence describes an *attractive* force between the two atoms. What is the angular dependency of this induced interaction? Show that it decays as $\sim 1/|\mathbf{R}|^6$.

c) Is the angular dependency in b) expected for two hydrogen atoms in their ground states? What is the expected behaviour? Write down the expression for $\Delta E(\mathbf{R})$ that one has to evaluate to meet these expectations if only states with principal quantum numbers $n \leq 2$ are taken into account. (It is not required to evaluate the matrix elements.)

Problem 2: Permutation operator (Oral)

Learning objective

In the lecture the concept of indistinguishable particles was introduced. The key operation in this context is the exchange or *permutation* of particles. In the mathematical framework of quantum mechanics, this process is described by the *permutation operator*. Here you derive some characteristic properties of this operator.

We consider a system of two particles in one spatial dimension. Let $\mathcal{H}^{(1)}$ and $\mathcal{H}^{(2)}$ be their respective Hilbert spaces and let $|x\rangle^{(i)}$ denote the position basis of $\mathcal{H}^{(i)}$. Then, the operator which exchanges the two particles in the product Hilbert space $\mathcal{H} = \mathcal{H}^{(1)} \otimes \mathcal{H}^{(2)}$ can be formally defined by its action on the product basis of two-particle states $|x_1 x_2\rangle \equiv |x_1\rangle^{(1)} \otimes |x_2\rangle^{(2)}$ by

$$P_{(12)} |x_1 x_2\rangle \equiv |x_2 x_1\rangle \tag{4}$$

for all $x_1, x_2 \in \mathbb{R}$. We call P_p the *permutation operator* corresponding to the permutation p. Here we only consider $p = (12)$.

Show that ...

a) $P_{(12)}^{-1} = P_{(12)}^{\dagger} = P_{(12)}$.

b) the eigenvalues of $P_{(12)}$ can only be $+1$ and -1.

c) the states

$$|x\rangle_A = |xx\rangle \tag{5a}$$

$$|x_1 x_2\rangle_B = \frac{1}{\sqrt{2}} \left(|x_1 x_2\rangle + |x_2 x_1\rangle \right) \tag{5b}$$

$$|x_1 x_2\rangle_C = \frac{1}{\sqrt{2}} \left(|x_1 x_2\rangle - |x_2 x_1\rangle \right) \tag{5c}$$

are eigenstates of $P_{(12)}$.

Problem 3: Identical fermions in a potential well (Oral)

> **Learning objective**
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> In the lecture you learned that the wave function of multiple fermions must be antisymmetric under the exchange of particles. Here you study the consequences of this rule by means of a simple toy model. In particular, you elaborate on the consequences of the antisymmetry in the presence of interactions between the fermions.

We consider two identical spin-$1/2$ fermions in a one-dimensional potential given by

$$V(x) = \begin{cases} 0 & |x| \leq 1 \\ \infty & \text{otherwise} . \end{cases} \tag{6}$$

The (dimensionless) single-particle Hamiltonian for the ith particle is given by

$$H^{(i)} = -\frac{1}{2}\partial_{x_i}^2 + V(x_i) . \tag{7}$$

a) Explain why we can treat the orbital motion and the spin dynamics separately, that is, explain why we can write the single-particle eigenstates as a product of orbital- and spin wave functions.

  Write down the orbital wave functions and eigenenergies of the two single-particle eigenstates that are lowest in energy.

b) Determine the ground state and the ground state energy of a two-fermion system with Hamiltonian $H = \sum_{i=1}^{2} H^{(i)}$ in the following two cases:

   i. For a spin state that is *antisymmetric* under exchange of the two fermions, i.e., the singlet state $(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)/\sqrt{2}$.

   ii. For a spin state that is *symmetric* under exchange of the two fermions, i.e., one of the triplet states $|\uparrow\uparrow\rangle$, $|\downarrow\downarrow\rangle$ or $(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)/\sqrt{2}$.

c) Examine the influence of a contact-interaction between the two fermions which is described by the interaction potential $\lambda\,\delta(x_1 - x_2)$ with strength $\lambda \in \mathbb{R}$. To this end, calculate the energy correction in first order perturbation theory (assuming $|\lambda| \ll 1$) for both the singlet state and the triplet states.

  Explain why the perturbative result for the triplet states is correct for arbitrary λ.