Prof. Dr. Hans-Peter Büchler
Institute for Theoretical Physics III, University of Stuttgart

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Problem 13.1: Pauli Matrices

[Oral] (4 pts.)

↪ `ID: ex_pauli_matrices:qm2122`

Learning objective

The Pauli matrices are very important for the description of two-level systems. In this exercise you will derive some useful properties of the Pauli matrices.

The Pauli matrices are

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{1}$$

a) Prove that the Pauli matrices fulfill the following commutation relation:

$$[\sigma_i, \sigma_j] = 2i\epsilon_{ijk}\sigma_k. \tag{2}$$

b) Show that

$$\sigma_i\sigma_j = \delta_{ij}\mathbb{1} + i\epsilon_{ijk}\sigma_k. \tag{3}$$

Use this relation to prove that

$$(\mathbf{r}\cdot\boldsymbol{\sigma})^2 = |\mathbf{r}|^2\mathbb{1}, \tag{4}$$

with $\boldsymbol{\sigma} = (\sigma_x, \sigma_y, \sigma_z)^T$.

c) For spin 1/2 the spin operator $\mathbf{S} = (S_x, S_y, S_z)^T$ can be written in terms of Pauli matrices $\mathbf{S} = \hbar/2\boldsymbol{\sigma}$. Show that the representation of the rotation takes the form

$$U_{\theta\hat{\mathbf{n}}} = \exp\left(-\frac{i}{\hbar}\theta\,\mathbf{S}\cdot\hat{\mathbf{n}}\right) = \mathbb{1}\cos\frac{\theta}{2} - i\boldsymbol{\sigma}\cdot\hat{\mathbf{n}}\sin\frac{\theta}{2}, \tag{5}$$

where $\hat{\mathbf{n}}$ is the rotation axis and θ the rotation angle.
Consider the state $|{\uparrow}\rangle = (1,0)^T$. What is the expectation value of the spin operator after rotation by $\pi/2$ and π around the y axis?

d) The density matrix of a two-level system can be written as

$$\rho = \frac{1}{2}(\mathbb{1} + \mathbf{r}\cdot\boldsymbol{\sigma}). \tag{6}$$

What are the conditions on $\mathbf{r}$? What are the conditions for pure states?

Problem Set Version: **1.0** | **qm2122**

Problem 13.2: Van der Waals interaction **[Written] (5 pts.)**

↪ ID: `ex_van_der_waals_interaction:qm2122`

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 $\boldsymbol{R}_A = \boldsymbol{0}$ and $\boldsymbol{R}_B = \boldsymbol{R}$ and large distance $|\boldsymbol{R}|$, so that the overlap of their charge distributions is negligible; The nuclei are much heavier and thus much slower than electrons, such that they can be assumed to be 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

$$H = H_A + H_B + H_{\text{int}}\,, \tag{7}$$

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

$$H_{\text{int}} = \frac{e^2}{|\boldsymbol{R}|} + \frac{e^2}{|\boldsymbol{R}+\boldsymbol{r}_B-\boldsymbol{r}_A|} - \frac{e^2}{|\boldsymbol{R}+\boldsymbol{r}_B|} - \frac{e^2}{|\boldsymbol{R}-\boldsymbol{r}_A|}\,, \tag{8}$$

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

$$H_{\text{int}} = \frac{1}{|\boldsymbol{R}|^3}\left[\boldsymbol{d}_A \cdot \boldsymbol{d}_B - \frac{3(\boldsymbol{d}_A \cdot \boldsymbol{R})(\boldsymbol{d}_B \cdot \boldsymbol{R})}{|\boldsymbol{R}|^2}\right] \tag{9}$$

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

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 $\boldsymbol{R}$ between the atoms fixed. Then, the energy correction $\Delta E(\boldsymbol{R})$ becomes parametrically dependent on the atom distance $\boldsymbol{R}$, which is interpreted as interaction between the atoms in the so called Born-Oppenheimer approximation.

a) Show that there is no contribution to $\Delta E(\boldsymbol{R})$ 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., $\langle e|_i\, \boldsymbol{d}_i\, |g\rangle_i = d/\sqrt{3}\, \boldsymbol{e}_z$ where $\boldsymbol{e}_z$ denotes the unit vector in z-direction.

b) Show that the second order contribution to $\Delta E(\boldsymbol{R})$ 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 $\sim 1/|\boldsymbol{R}|^6$.

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 $\Delta E(\boldsymbol{R})$ that one has to evaluate to meet these expectations if only states with principal quantum numbers $n = 2$ are taken into account. (It is not required to evaluate the matrix elements.)

You will now evaluate $\Delta E(\mathbf{R})$ taking into account all states with principal quantum number $n = 2$.

d) Determine all relevant matrix elements of the dipole operator.

e)* Use your results from d) to calculate $\Delta E(\mathbf{R})$.

Hint: Introduce a new eigenbasis for the Hamiltonian H_A (and H_B) by replacing $|21 \pm 1\rangle_A$ and $|210\rangle_A$ with

$$|x_A\rangle = -\frac{|21+1\rangle_A - |21-1\rangle_A}{\sqrt{2}}, \quad |y_A\rangle = i\frac{|21+1\rangle_A + |21-1\rangle_A}{\sqrt{2}}, \quad |z_A\rangle = |210\rangle_A . \quad (10)$$

Why is this possible? Write down the matrix elements $\langle x_A| \boldsymbol{d}_A |g_A\rangle$,$\langle y_A| \boldsymbol{d}_A |g_A\rangle$ and $\langle z_A| \boldsymbol{d}_A |g_A\rangle$.