5^{th} Exercise sheet for Advanced Quantum Mechanics in WS16

Second-Order Perturbation Theory

Exercise 12 *Review of second-order perturbation theory (the non-degenerate case)*

In Exercise 10 we considered Rayleigh–Schrödinger perturbation theory up to first order and derived the corresponding energy shift for both the non-degenerate and the degenerate case. In this exercise we extend this perturbative ansatz up to second order in energy.

a) Assume that the eigenkets $|\Psi_a\rangle$ of the unperturbed Hamiltonian H_0 are non-degenerate. It is convenient to choose

$$\langle \Psi_a | \Psi_a' \rangle = 1. \tag{1}$$

Derive an explicit form of the perturbed eigenkets $|\psi_{a,1}\rangle$ in the basis of non-perturbed eigenkets $|\Psi_a\rangle$.

b) Extend the perturbative ansatz described in Eqs. (2) and (3) of Exercise 10 up to order $\mathcal{O}(\epsilon^2)$ and derive the corresponding second-order energy shift $E_{a,2}$.

Exercise 13 *Application: Linear and quadratic Stark effect*

Consider a hydrogen-like atom in a homogeneous electric field which is oriented along the positive z-axis. We will assume a sufficiently strong electric field so that spin effects, atomic fine structure, and other corrections can be neglected so that the unperturbed Hamiltonian reads

$$H_0 = \frac{\mathbf{p}^2}{2m_e} - \frac{Ze^2}{r}, \tag{2}$$

where m_e denotes the mass of the electron, and the perturbation Hamiltonian is

$$H_1 = e|\mathbf{E}|z. \tag{3}$$

The unperturbed energy eigenstates $|nlm\rangle$ are eigenstates of the operators $\mathbf{L}^2$ and L_z, with their eigenvalues $l = 0, 1, \ldots$ and $m = -l, \ldots, l$, respectively.

a) Calculate the first-order energy shift $\Delta E^{(1)}_{nlm}$ of a general s state ($l = 0$).

b) Calculate the first-order energy shift $\Delta E^{(1)}_{nlm}$ for the first excited state ($n = 2$).

c) Calculate the upper and lower bound of the second-order energy shift $\Delta E^{(2)}_{100}$ of the ground state.

Hint: Derive selection rules for the matrix element $\langle n', l', m' | z | n, l, m \rangle$.

Useful formulas for Ex. 13 *Radial wave functions, spherical harmonics and Clebsch–Gordan coefficients*

Radial wave functions:

$$R_{10} = 2\left(\frac{Z}{a}\right)^{3/2} e^{-Zr/a}, \quad R_{20} = 2\left(\frac{Z}{2a}\right)^{3/2}\left(1-\frac{Zr}{2a}\right) e^{-Zr/2a}, \tag{4}$$

$$R_{21} = \frac{1}{\sqrt{3}}\left(\frac{Z}{2a}\right)^{3/2} \frac{Zr}{a} e^{-Zr/2a}. \tag{5}$$

Spherical harmonics of rank 0 and 1:

$$Y_0^0(\theta,\varphi) = \frac{1}{2}\sqrt{\frac{1}{\pi}}, \quad Y_1^{-1}(\theta,\varphi) = \frac{1}{2}\sqrt{\frac{3}{2\pi}}, \tag{6}$$

$$Y_1^0(\theta,\varphi) = \frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta, \quad Y_1^1(\theta,\varphi) = \frac{-1}{2}\sqrt{\frac{3}{2\pi}}\,\sin\theta\, e^{i\varphi}. \tag{7}$$

Integral over 3 spherical harmonics:

$$\int_{4\pi} Y_{\ell_1}^{m_1 *}(\Omega) Y_{\ell_2}^{m_2 *}(\Omega) Y_L^M(\Omega)\, d\Omega = \sqrt{\frac{(2\ell_1+1)(2\ell_2+1)}{4\pi(2L+1)}}\langle \ell_1\, 0\, \ell_2\, 0 | L\, 0\rangle \langle \ell_1\, m_1\, \ell_2\, m_2 | L\, M\rangle. \tag{8}$$

Selection rule:

$$\langle \ell_1\, m_1\, \ell_2\, m_2 | L\, M\rangle \neq 0 \quad \text{if} \begin{cases} M = m_1 + m_2, , \\ |l_1 - l_2| \leq L \leq l_1 + l_2, \\ l_1 + l_2 + L \in \mathbb{Z}. \end{cases} \tag{9}$$

Explicit form of Clebsch–Gordan coefficients ($l_2 = 1, m_2 = 0$):

$$\langle l_1\, m\, 1\, 0 | (l_1+1)\, m\rangle = \sqrt{\frac{(l_1-m+1)(l_1+m+1)}{(2l_1+1)(l_1+1)}}, \tag{10}$$

$$\langle l_1\, m\, 1\, 0 | l_1\, m\rangle = \frac{m}{\sqrt{l_1(l_1+1)}}, \tag{11}$$

$$\langle l_1\, m\, 1\, 0 | (l_1-1)\, m\rangle = -\sqrt{\frac{(l_1-m)(l_1+m)}{l_1(2l_1+1)}}. \tag{12}$$