Ex6220: Second order perturbation of an atom in electric field

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The problem:

(1) Explain why, in a generic way, an electron eigenfunction, in an atom, has a defined parity. How does the above explains that in an electric field the first order correction to the energy is zero. An atom can be described as a two level system with level spacing Δ.
(2) Write the Hamiltonian of an atom in electric field.
Use ε for the perturbation strength. What is the connection of ε with the strength of the electric field f?
(3) Using the perturbation theory, find the second order correction to the energy of the atom above. Compare the solution to the exact solution from the diagonalization of the Hamiltonian. Be sure you understand the following: An electric field can change in different places in space. That is why an atom will feel an effective potential $V(R) \propto |\varepsilon(R)|^2$ This potential explains the energy drop caused by the atom's polarization in electric field.
(4) Define and calculate the polarization P using perturbation theory, by expanding the wavefunction to first order correction.
Make sure that the result is giving the same polariztion coefficient α, as the one that is implied on the previous question.

The solution:

(1) Electron in an atom has $r \longrightarrow -r$ symmetry, thus has a definite parity.
As a result $\langle \hat{x} \rangle = \langle \hat{y} \rangle = \langle \hat{z} \rangle = 0$, and since $V(\hat{x}) = -ef\hat{x}$, it follows that $\langle V(\hat{x}) \rangle = 0$.
Consequently the first order correction is zero.

(2) The Hamiltonian is:

$$H = H_0 + V$$

H_0 can be written in the $|S\rangle, |A\rangle$ basis as follows:

$$H_0 = \begin{pmatrix} 0 & 0 \\ 0 & \Delta \end{pmatrix}$$

We may subtract constant from H_0 so we could write it in terms of σ_z:

$$H_0 = \begin{pmatrix} -\Delta/2 & 0 \\ 0 & \Delta/2 \end{pmatrix} = -\frac{\Delta}{2}\sigma_z$$

Now we will write $V(\hat{x}) = -ef\hat{x}$ in terms of H_0 basis:

$$V = \begin{pmatrix} 0 & ef/2 \\ ef/2 & 0 \end{pmatrix} = \frac{ef}{2}\sigma_x$$

Let us define the perturbation strength as $\varepsilon = ef/2$, so that we may write the Hamiltonian as:

$$\mathcal{H} = \begin{pmatrix} -\Delta/2 & \varepsilon \\ \varepsilon & \Delta/2 \end{pmatrix}$$

(3) By using the formula derived in class:

$$E_0 = E_0^{[0]} + V_{nn} + \sum_{m \neq n} \frac{|V_{nm}|^2}{E_n^{[0]} - E_m^{[0]}}$$

We obtain the atoms energy, in the ground state, up to the second order:

$E_0^{[0]} = -\frac{\Delta}{2}$

$E_0^{[1]} = 0$

$E_0^{[2]} = -\frac{|ef|^2}{4\Delta}$

Now we may write: $E_0 = E_0^{[0]} + E_0^{[1]} + E_0^{[2]} = -\frac{\Delta}{2} - \frac{|ef|^2}{4\Delta}$.

To compare the result with the exact solution, we first diagonalize the Hamiltonian:

$$\mathcal{H}_{diag} = \begin{pmatrix} -\sqrt{(\frac{\Delta}{2})^2 + (\frac{ef}{2})^2} & 0 \\ 0 & \sqrt{(\frac{\Delta}{2})^2 + (\frac{ef}{2})^2} \end{pmatrix}$$

Hence the ground state energy is:

$E_{exact} = -\sqrt{(\frac{\Delta}{2})^2 + (\frac{ef}{2})^2}$

By Taylor expansion of E_{exact} we can see that both terms coincide:

$E_{exact} = -\sqrt{(\frac{\Delta}{2})^2 + (\frac{ef}{2})^2} \approx -\frac{\Delta}{2} - \frac{|ef|^2}{4\Delta}$

(4) Let us define the perturbed ground state as $|\psi_0\rangle$, and now we shall write the wave function corrections using:

$$|\psi_n\rangle = |\psi_n^{[0]}\rangle + \sum_{m \neq n} \frac{\langle \psi_m | V_{nm} | \psi_n \rangle}{E_n^{[0]} - E_m^{[0]}} |\psi_m\rangle$$

We obtain:

$$|\psi_0\rangle = |S\rangle + \frac{ef}{2\Delta}|A\rangle$$

The polarization is $P = \alpha f$, thus the polarizability is given by $\alpha = \frac{e}{f}\hat{x}$, now we will write it in terms of $|S\rangle, |A\rangle$ basis:

$$\alpha = \frac{e}{f}\sigma_x$$

At last we calculate the expectation value of the above term with our perturbed state:

$$\langle \alpha \rangle = \frac{e}{f}\langle \psi_0 | \sigma_x | \psi_0 \rangle = \frac{e^2 f}{2\Delta}$$

We can compare it with the result from the perturbed energy as $E = \frac{\alpha f^2}{2}$ so that we may get:

$$\langle \alpha \rangle = \frac{e^2 f}{2\Delta}$$

So both results coincide.