

Ex6220: Perturbation theory for the Hydrogen atom in electric field - Stark effect

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The problem:

Stark effect regards to the splitting of the spectrum of atoms and molecules. Assume a Hydrogen atom with a spin-less electron is placed in a homogeneous electric field $\mathbf{E} = f\hat{z}$. It is assumed the probability to find the electron in states of $\nu \geq 3$ is zero.

- (1) Write the Hamiltonian $\mathcal{H} = \mathcal{H}_0 + V$ for the system.
- (2) Explain why due to parity the first order correction of the energy vanishes under perturbation theory, does it matter whether the field been in some other direction? What would be your answer if the hydrogen atom was asymmetric diatom molecule?(Hint: you may use the spherical harmonics parity properties).
- (3) Explain in what cases the hydrogen atom can react with the electric field like a symmetric diatom molecule. This is called linear Stark effect, and we can say the system has a "constant" dipole moment.

We now assume the electron is in the ground state.

- (4) Write \mathcal{H} in the unperturbed basis, what can you say about the symmetry of the orbital and the diagonal of \mathcal{H} ?
- (5) Explain why under perturbation theory the leading order of the correction is determined by a certain orbital. Show it can be described as a two site system with energy difference Δ and perturbation strength ϵ . You may leave ϵ as an integral over the wave functions. Why we can treat the problem as a two sites problem? Define the sites and the effective distance between sites.
- (6) Find the energy eigenvalue of the ground state using perturbation theory up to the 2nd order and by direct calculation. Are there differences?
- (7) Find the ground state eigenstate using perturbation theory up to first order on the wave function, find the polarization of the electron in that state, the polarization coefficient α and compare the solution to the polarization coefficient that can be found using the relation between the energy and the electric field.

Given: $Y^{0,0} = \frac{1}{\sqrt{4\pi}}$, $Y^{1,-1} = \sqrt{\frac{3}{8\pi}} \sin\theta e^{-i\phi}$, $Y^{1,0} = \sqrt{\frac{3}{4\pi}} \cos\theta$, $Y^{1,1} = -\sqrt{\frac{3}{8\pi}} \sin\theta e^{i\phi}$.

The solution:

- (1) The external electric field described by the potential $V = -efz = -efr \cos\theta$, therefore we can write

$$\mathcal{H} = \mathcal{H}_0 + V = \frac{p^2}{2M} - efr \cos\theta. \quad (1)$$

The basis of \mathcal{H}_0 on a spherical surface decomposes to the spherical harmonics basis $|\nu, l, m\rangle$. It is given the only blocks we shall be interested with are the $l = 0, l = 1$ blocks.

- (2) For a given perturbation z we calculate the first order energy correction by:

$$\langle \Psi_i | z | \Psi_i \rangle = \int_{-\infty}^{\infty} \Psi_i^* z \Psi_i dz. \quad (2)$$

Where since spherical harmonics have $|r\rangle \rightarrow |-r\rangle$ parity we take the integral from $(-\infty)$.

$$\int_{-\infty}^0 \Psi_i^* z \Psi_i dz + \int_0^{\infty} \Psi_i^* z \Psi_i dz = \int_0^{\infty} \Psi_i^*(-z) \Psi_i dz + \int_0^{\infty} \Psi_i^* z \Psi_i dz = 0. \quad (3)$$

We can see the only way the integral is non zero is when the function $\Psi_i^* \Psi_i$ is odd. The spherical harmonics parity $Y^{l,m}(-r) = (-1)^l Y^{l,m}(r)$ dictates that in our case $\Psi_i^* \Psi_i$ is always even, hence we conclude the diagonal is 0 and the direction of the electric field does not change the result. In the case of asymmetric diatom molecule we have one atom with higher probability to host the electron than the other atom. As a consequence the molecule has a natural dipole moment, we lose the spherical symmetry, and therefore losing the parity.

(3) When the electron in the Hydrogen atom is placed in initial state at a $|2, l, 0\rangle$ state there is a coupling between the states $|2, 0, 0\rangle$ and $|2, 1, 0\rangle$, but their unperturbed energy is the same, therefore we have a degenerate state. Since we have a degenerate state we cannot use perturbation theory and we have to diagonalize this block, resulting in two different energies linear in ϵ , with eigenstates of being polarized in to or away from the field. This is linear Stark effect.

(4) For calculating the perturbation matrix elements we write the perturbation in $|\nu, l, m\rangle$ basis:

$$\begin{aligned}
\cos\theta &= \sqrt{\frac{4\pi}{3}} Y^{1,0} \rightarrow V = -efr \sqrt{\frac{4\pi}{3}} Y^{1,0}. \\
-ef \sqrt{\frac{4\pi}{3}} \langle 1, 0, 0 | r Y^{1,0} | 2, 0, 0 \rangle &= -\frac{ef}{\sqrt{3}} \langle 1, 0, 0 | r | 2, 0, 0 \rangle = 0. \\
-ef \sqrt{\frac{4\pi}{3}} \langle 1, 0, 0 | r Y^{1,0} | 2, 1, -1 \rangle &= -\frac{ef}{\sqrt{3}} \langle 1, 0, 0 | r | 2, 1, -1 \rangle = 0. \\
-ef \sqrt{\frac{4\pi}{3}} \langle 1, 0, 0 | r Y^{1,0} | 2, 1, 0 \rangle &= -\frac{ef}{\sqrt{3}} \langle 1, 0, 0 | r | 2, 1, 0 \rangle = -\frac{efC_1}{\sqrt{3}}. \\
-ef \sqrt{\frac{4\pi}{3}} \langle 1, 0, 0 | r Y^{1,0} | 2, 1, 1 \rangle &= -\frac{ef}{\sqrt{3}} \langle 1, 0, 0 | r | 2, 1, 1 \rangle = 0.
\end{aligned} \tag{4}$$

Finally we can write the Hamiltonian. Noting the unperturbed energies $E_{\nu,l,m} = \frac{M\alpha^2}{2(l+\nu)^2}$, (taking $\alpha = 1$ for convenience):

$$\begin{aligned}
\mathcal{H} &= \mathcal{H}_0 + V = \\
&\begin{pmatrix} M/2 & 0 & 0 & 0 & 0 \\ 0 & M/18 & 0 & 0 & 0 \\ 0 & 0 & M/18 & 0 & 0 \\ 0 & 0 & 0 & M/18 & 0 \\ 0 & 0 & 0 & 0 & M/18 \end{pmatrix} + \begin{pmatrix} 0 & 0 & -efC_1/\sqrt{3} & 0 & 0 \\ 0 & 0 & -efC_2/\sqrt{3} & 0 & 0 \\ -efC_1/\sqrt{3} & -efC_2/\sqrt{3} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix}. \tag{6}
\end{aligned} \tag{5}$$

We can see that if the electron has been set at the ground state the perturbation couples the states: $|1, 0, 0\rangle$ and $|2, 1, 0\rangle$.

(5) We have left the radial integrals as $C_1 = \int_0^\infty R^{l',1*} r^3 R^{l,1} dr$ and $C_2 = \int_0^\infty R^{l',2*} r^3 R^{l,2} dr$. In general the perturbation will continue to other $|\nu \geq 3, l = l' \pm 1, 0\rangle$ states, but the perturbation magnitude is much smaller, so we can set $\nu = 2$ as the leading order of the perturbation. In a more practical sense the dynamics is reduced to a two sites system with the electron jumps between the two states $|1, 0, 0\rangle$ and $|2, 1, 0\rangle$ with transition amplitude $\epsilon = -efC_1/\sqrt{3}$ and energy difference $\Delta = M/2 - M/18$. The key observation is that we defined the electric potential as $V = -efz$ referring to the electric potential as the position basis $\sim \sigma_z$ and the orbitals energy as the perturbation $\sim \sigma_x$, the Hamiltonian would look like:

$$\mathcal{H} = \begin{pmatrix} \epsilon & 0 \\ 0 & -\epsilon \end{pmatrix} + \begin{pmatrix} 0 & \Delta/2 \\ \Delta/2 & 0 \end{pmatrix} = \begin{pmatrix} \epsilon & \Delta/2 \\ \Delta/2 & -\epsilon \end{pmatrix} \rightarrow \sigma_z \text{ basis.} \tag{7}$$

We then define the orbitals as the position basis $\sim \sigma_z$ and the electric potential as the perturbation $\sim \sigma_x$, and then:

$$\mathcal{H} = \begin{pmatrix} \Delta/2 & 0 \\ 0 & -\Delta/2 \end{pmatrix} + \begin{pmatrix} 0 & \epsilon \\ \epsilon & 0 \end{pmatrix} = \begin{pmatrix} \Delta/2 & \epsilon \\ \epsilon & -\Delta/2 \end{pmatrix} \rightarrow \sigma_x \text{ basis.} \quad (8)$$

(6) Noting the symmetric and anti-symmetric states as "0" and "1", and using formulas derived in class for second order perturbation approximation we find the ground state energy:

$$\begin{aligned} E_0^{[0]} &= -\frac{\Delta}{2}. \\ E_0^{[2]} &= \frac{|V_{0,1}|^2}{E_0^{[0]} - E_1^{[0]}} = -\frac{\epsilon^2}{\Delta}. \\ E_0 &\sim -\frac{\Delta}{2} - \frac{\epsilon^2}{\Delta}. \end{aligned} \quad (9)$$

We can find the Eigenenergies with direct and accurate calculation as well by diagonalizing the Hamiltonian:

$$\begin{vmatrix} \Delta/2 - \lambda & \epsilon \\ \epsilon & -\Delta/2 - \lambda \end{vmatrix} \rightarrow \lambda = \pm \sqrt{\frac{\Delta^2}{4} + \epsilon^2}. \quad (10)$$

By Taylor approximation we see

$$\lambda_- = -\frac{\Delta}{2} \sqrt{1 + \frac{4\epsilon^2}{\Delta^2}} \sim -\frac{\Delta}{2} - \frac{\epsilon^2}{\Delta}. \quad (11)$$

(7) For finding the first order approximation for the wave function we will use the according formula found in class (in the σ_x basis).

$$|\Psi_0\rangle = |\Psi_0^0\rangle + \frac{V_{0,1}}{E_0^{[0]} - E_1^{[0]}} |\Psi_1^{[0]}\rangle = \begin{pmatrix} 1 \\ \epsilon/\Delta \end{pmatrix}. \quad (12)$$

We are now ready to find the polarization:

$$\langle P \rangle = \langle \Psi_0 | \sigma_x | \Psi_0 \rangle = -\frac{\partial}{\partial \epsilon} \left[(1 \quad \epsilon/\Delta) \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ \epsilon/\Delta \end{pmatrix} \right] = 2\frac{\epsilon}{\Delta}. \quad (13)$$

Since $\langle P \rangle = \langle \alpha \rangle \epsilon$ we can derive $\langle \alpha \rangle = \frac{\partial \langle P \rangle}{\partial \epsilon} = \frac{2}{\Delta}$.

We can easily confirm the solution by:

$$E_0 = -\frac{\alpha \epsilon^2}{2} \rightarrow \alpha = -\frac{\partial^2 E_0}{\partial \epsilon^2} \Big|_{\epsilon=0} = \frac{\partial^2}{\partial \epsilon^2} \left(\frac{\Delta}{2} + \frac{\epsilon^2}{\Delta} \right) \Big|_{\epsilon=0} = \frac{2}{\Delta}. \quad (14)$$

Which yields the same solution. This is the second order Stark effect.