

Solution 6

1.(a) If Hamiltonian is invariant under space inversion, then ¹

$$IH = HI. \tag{1}$$

Suppose $|\Psi\rangle$ is a non-degenerate eigenstate of H , say,

$$H|\Psi\rangle = E|\Psi\rangle.$$

We can construct one symmetrical state and also one antisymmetrical state,

$$|\Psi\rangle_s = |\Psi\rangle + I|\Psi\rangle, |\Psi\rangle_a = |\Psi\rangle - I|\Psi\rangle,$$

such that

$$H|\Psi\rangle_s = H|\Psi\rangle + HI|\Psi\rangle = H|\Psi\rangle + IH|\Psi\rangle = E|\Psi\rangle_s.$$

Therefore $|\Psi\rangle_s$ is an eigenstate of H with the eigenvalue E . It is easy to verify that $|\Psi\rangle_a$ is also an eigenstate of H with the same eigenvalue. Since there is no degeneracy of the eigenvalue E , so $|\Psi\rangle_s$ can differ from $|\Psi\rangle_a$ just by a factor. But they have different parities, so one of the them is zero. If $|\Psi\rangle_s$ is zero, then $I|\Psi\rangle = -|\Psi\rangle$. Otherwise $|\Psi\rangle_a$ is zero and $I|\Psi\rangle = |\Psi\rangle$.

(b). The first order perturbation theory expression is

$$\Delta E = -\langle\Psi|\varepsilon \cdot (\sum_i q_i \mathbf{r}_i)|\Psi\rangle.$$

Insert the trivial operator I^2 ,

$$\Delta E = -\langle\Psi|I^2\varepsilon \cdot (\sum_i q_i \mathbf{r}_i)I^2|\Psi\rangle$$

From (a), $|\Psi\rangle$ has definitive parity c (1 or -1),

$$I|\Psi\rangle = c|\Psi\rangle, \langle\Psi|I = \langle\Psi|c.$$

So

$$\Delta E = -c^2\langle\Psi|I\varepsilon \cdot (\sum_i q_i \mathbf{r}_i)I|\Psi\rangle = -\langle\Psi|I\varepsilon \cdot (\sum_i q_i \mathbf{r}_i)I|\Psi\rangle.$$

¹The parity operator I is unitary and $I^2 = 1$.

Because \mathbf{r} is a vector operator, $I\mathbf{r}I = -\mathbf{r}$.

$$\Delta E = \langle \Psi | I\boldsymbol{\varepsilon} \cdot (\sum_i q_i \mathbf{r}_i) I | \Psi \rangle = -\Delta E.$$

It follows that the first order perturbation $\Delta E = 0$.

1.(c) From (b), we know that the expected value of dipole operator for any state with definitive parity is zero. Therefore if there is no degeneracy of states with different parities, based on the non-degenerate perturbation theory, the first order correction vanishes. In the other word, the energy shift is not linear in the applied field. However, there could be some quasi-degenerate states with tiny energy gaps. When the energy shifting induced by the applied field is larger than the energy gap, we should treat them as degenerate states and use the degenerate perturbation theory. And if the quasi-degenerate states have different parities, we may get first order correction (linear in the applied field).

There are many vibrational and rotational states of the water molecule. However, the energy gap of vibrational states is larger than rotational states, so we focus on the rotational states and try to find the smallest energy gap between two states with different parities. The water molecule is V-shaped and the the largest moment of inertia I is along the line perpendicular to the plane of the water molecule. Because the mass center is very close to the oxygen atom, the moment of inertia could be estimated as

$$I = 2m_p r^2 = 3.1 \times 10^{-47} \text{kg} \cdot \text{m}^2$$

where m_p is the mass of proton and $r = 0.9584\text{\AA}$ is the bond length. The ground state and the excited rotational states have different parities and the energy gap between them is

$$\frac{\hbar^2}{2I} = 1.8 \times 10^{-22} \text{J}$$

On the other hand, the magnitude of energy shifting could be estimated by,

$$p \cdot \boldsymbol{\varepsilon}$$

$p = 6.2 \times 10^{-30} \text{C} \cdot \text{m}$ is the electric dipole of the water molecule. Let $p \cdot \boldsymbol{\varepsilon} < \frac{\hbar^2}{2I}$, we should have

$$\boldsymbol{\varepsilon} < 2.9 \times 10^7 \text{V} \cdot \text{m}^{-1}.$$

2.(a) Without perturbation, the Hamiltonian is

$$H_0 = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}).$$

Here

$$V(\mathbf{r}) = \begin{cases} 0 & r < R_0 \\ V_0 & r \geq R_0 \end{cases}.$$

After perturbation, the potential becomes

$$V'(\mathbf{r}) = \begin{cases} 0 & r < R_0 + \Delta R(\hat{\mathbf{r}}) \\ V_0 & r \geq R_0 + \Delta R(\hat{\mathbf{r}}) \end{cases}.$$

Write $H_{int} = V' - V$.

$$H_{int}(r, \hat{\mathbf{r}}) = \begin{cases} -V_0 & R_0 \leq r < R_0 + \Delta R(\hat{\mathbf{r}}), \Delta R(\hat{\mathbf{r}}) > 0 \\ V_0 & R_0 + \Delta R(\hat{\mathbf{r}}) \leq r < R_0, \Delta R(\hat{\mathbf{r}}) < 0 \\ 0 & otherwise \end{cases}.$$

If $\Delta R(\hat{\mathbf{r}}) > 0$, Let $f_{\Delta R(\hat{\mathbf{r}})}(r) = H_{int}(r, \hat{\mathbf{r}})/(-V_0\Delta R(\hat{\mathbf{r}}))$. Then for any continuous function $h(r)$, it is evident that

$$\lim_{\Delta R(\hat{\mathbf{r}}) \rightarrow 0} \int_{-\infty}^{\infty} dr f_{\Delta R(\hat{\mathbf{r}})}(r) h(r) = h(R_0).$$

It implies that

$$\lim_{\Delta R(\hat{\mathbf{r}}) \rightarrow 0} f_{\Delta R(\hat{\mathbf{r}})}(r) = \delta(r - R_0),$$

or

$$\lim_{\Delta R(\hat{\mathbf{r}}) \rightarrow 0} H_{int}(r, \hat{\mathbf{r}}) = -V_0\Delta R(\hat{\mathbf{r}})\delta(r - R_0).$$

The same result holds for the case $\Delta R(\hat{\mathbf{r}}) < 0$.

(b) Assume there is no shift of the bubble and $V_0 \rightarrow \infty$. From assignment 4, we know the p-state wavefunctions ($m = -1, 0, 1$) are

$$\Psi_m(\mathbf{r}) = \begin{cases} Aj_1(kr)Y_{1m}(\hat{\mathbf{r}}) & r \leq R_0 \\ 0 & r > R_0 \end{cases}.$$

where $kR_0 \approx a_1 = 4.49$ is the first zero of j_1 . We need to determine the normalization constant A , (adjusted to be positive)

$$A^2 \int_0^{R_0} r^2 j_1^2(kr) = 1.$$

By the first identity,

$$-A^2 \frac{a_1^3}{2k^3} j_0(a_1) j_2(a_1) = 1.$$

Then by the second identity, $j_0(a_1) = -j_2(a_1)$. Since $j_0(a_1) < 0$,

$$A = -\sqrt{\frac{2}{R_0^3} \frac{1}{j_0(a_1)}}$$

Therefore by the third identity,

$$\frac{\partial \Psi_m}{\partial r} \Big|_{r=R_0} = Ak j_0(a_1) Y_{1m}(\hat{\mathbf{r}}) = -\sqrt{\frac{2}{R_0^3}} k Y_{1m}(\hat{\mathbf{r}}).$$

(c) Now V_0 is finite, so the partial derivative of Ψ_m about r at R_0 should be continuous. By the good approximation the right-hand derivative is,

$$\frac{\partial}{\partial r} \Big|_{r \rightarrow R_0^+} \Psi_m(r, \hat{\mathbf{r}}) \approx -K \Psi_m(R_0, \hat{\mathbf{r}}).$$

The left-hand derivative is close to the result in (b),

$$\frac{\partial}{\partial r} \Big|_{r \rightarrow R_0^-} \Psi_m(r, \hat{\mathbf{r}}) \approx -\sqrt{\frac{2}{R_0^3}} k Y_{1m}(\hat{\mathbf{r}}).$$

Compare the two sides, we get

$$\Psi_m(R_0, \hat{\mathbf{r}}) \approx \sqrt{\frac{2}{R_0^3}} \frac{k}{K} Y_{1m}(\hat{\mathbf{r}}).$$

Since $(\hbar K)^2/2m = V_0 - E_1$ and $(\hbar k)^2/2m = E_1$,

$$\Psi_m(R_0, \hat{\mathbf{r}}) \approx \sqrt{\frac{2}{R_0^3} \left(\frac{E_1}{V_0 - E_1} \right)} Y_{1m}(\hat{\mathbf{r}}).$$

(d) We need to compute the matrix element of H_{int} ,

$$\langle n|H_{int}|m\rangle = \int d\Omega \int_0^\infty r^2 dr \Psi_n^*(r, \hat{\mathbf{r}}) H_{int}(r, \hat{\mathbf{r}}) \Psi_m(r, \hat{\mathbf{r}}).$$

Let $H_{int}(r, \hat{\mathbf{r}}) = -\epsilon V_0 P_2(\cos \theta) \delta(r - R_0)$ and integrate over r first, and we get

$$-\epsilon \frac{2V_0 E_1}{R_0(V_0 - E_1)} \int d\Omega Y_{1n}^*(\hat{\mathbf{r}}) Y_{1m}(\hat{\mathbf{r}}) P_2(\cos \theta)$$

Put in $P_2(\cos \theta) = -1/2 + 3 \cos^2 \theta/2$,

$$\begin{aligned} \langle 1|H_{int}|1\rangle &= \langle -1|H_{int}| - 1\rangle = \epsilon \frac{2V_0 E_1}{5R_0(V_0 - E_1)}, \\ \langle 0|H_{int}|0\rangle &= -\epsilon \frac{4V_0 E_1}{5R_0(V_0 - E_1)}. \end{aligned} \quad (2)$$

where the other elements are zero. Therefore the state $m = 0$ becomes non-degenerate.

(e) For $m = 0$ state, the energy will be lower when $\epsilon > 0$ (prolate).

$$F = \Delta E_1(\epsilon)/\epsilon = -\frac{4V_0 E_1}{5R_0(V_0 - E_1)} \approx -1.76 \times 10^{-11} N = -17.6 \text{ pN}.$$