

Assignment 6

In this assignment you will first prove that electric dipole moments are impossible and then reconcile this with the physical phenomenon of molecules such as H₂O. The second problem features the Jahn-Teller effect in photoexcited electron bubbles. This assignment is due Wednesday, October 10, in lecture.

1. The Hamiltonian H for ordinary matter, say a molecule, is invariant under space inversion. In the coordinate representation this amounts to the fact that under the transformation $\mathbf{r} \rightarrow -\mathbf{r}$ of all particle coordinates, H is unchanged. An important consequence of this is the fact that if $|\Psi\rangle$ is an eigenstate of H , then so is $I|\Psi\rangle$, where I is the inversion operator.

(a) Show that if $|\Psi\rangle$ is a **non-degenerate** eigenstate of H , then either $I|\Psi\rangle = +|\Psi\rangle$ or $I|\Psi\rangle = -|\Psi\rangle$.

Hint: Use symmetry projection with the representations $\chi_+(I) = 1$ and $\chi_-(I) = -1$ to construct states of definite inversion symmetry (symmetric and antisymmetric). Are you really able to construct *two* such states?

(b) The energy shift of a non-degenerate state $|\Psi\rangle$, linear in the applied electric field \mathcal{E} , is given by the first order perturbation theory expression

$$\Delta E = -\langle\Psi|\mathcal{E} \cdot \left(\sum_i q_i \mathbf{r}_i\right)|\Psi\rangle,$$

where q_i is the charge of the particle with coordinate \mathbf{r}_i . From what you learned in (a) argue that $\Delta E = 0$.

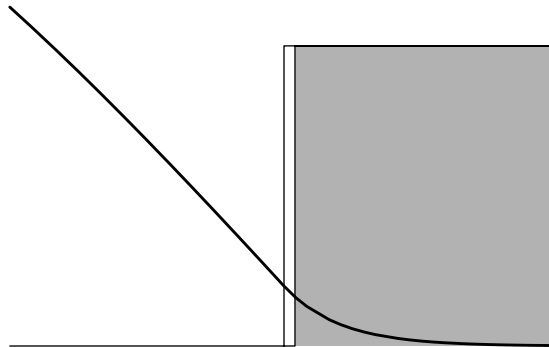
(c) As you certainly know, there are molecules with “permanent” electric dipole moments whose energy varies linearly with an applied electric field. Reconcile this with what you demonstrated above. Identify some quasi-degenerate states of molecules to explain why molecules can appear to have an electric dipole moment. In the case of H₂O make a rough estimate of the magnitude of \mathcal{E} below which the energy shift would no longer be linear in \mathcal{E} .

Hint: The key here is understanding the role of degeneracy. In lecture this theme arose in the discussion of the $n = 2$ states of hydrogen. Would there have been a linear energy shift (with respect to \mathcal{E}) had we used for our unperturbed states not the eigenstates of the usual hydrogen Hamiltonian H_0 , but the Hamiltonian $H_1 = H_0 + H_{fs}$ which includes “fine structure” terms? Whereas H_{fs} is also invariant with

respect to inversion, what matters here is that it removes the degeneracy of the 2s and 2p states. On the other hand, would the small degeneracy-breaking produced by H_{fs} even be noticed when the electric field perturbation is large?

2. In assignment 4 you found that the ground state electron in a spherical helium bubble can be photoexcited to any of three p-states. Here you will explore how the Jahn-Teller effect leads to a spontaneous deformation of the bubble that splits the degeneracy of these states.

Consider a shift of the bubble wall relative to the 1s equilibrium radius R_0 . The shift can in general vary in magnitude and sign over the surface of the bubble: $R(\hat{\mathbf{r}}) = R_0 + \Delta R(\hat{\mathbf{r}})$. We will model the helium as a continuum medium that imposes a *finite* potential barrier V_0 to the electron. As shown in the diagram, the electron wavefunction has a rapidly decaying tail into the helium. This detail is important, since it is through the small non-zero value of the wavefunction at the bubble surface that the bubble deformation manifests itself as a perturbation.



- (a) Show that for an infinitesimal shift ΔR , the perturbation is given by the expression

$$H_{\text{int}} = -V_0 \Delta R(\hat{\mathbf{r}}) \delta(r - R_0) .$$

Hint: This operator represents the difference of step potentials, as shown in the diagram.

The next two parts will prepare you to calculate matrix elements of this perturbation.

- (b) In the limit $V_0 \rightarrow \infty$, the p-state wavefunctions ($m = -1, 0, 1$) in the spherical bubble are

$$\Psi_m(\mathbf{r}) = A j_1(kr) Y_{1m}(\hat{\mathbf{r}}) ,$$

where $kR_0 \approx 4.49$ is the first zero of j_1 and A is a normalization constant. The energy of a p-state electron is $E_1 = (\hbar k)^2 / 2m_e$.

Show that (still in the limit $V_0 \rightarrow \infty$)

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

Hint: Here are three useful identities:

$$\int j_l^2(s) s^2 ds = \frac{1}{2} s^3 (j_l^2(s) - j_{l-1}(s) j_{l+1}(s))$$

$$j_{l+1}(s) = \left(\frac{2l+1}{s} \right) j_l(s) - j_{l-1}(s)$$

$$\frac{d}{ds} j_l(s) = j_{l-1}(s) - \left(\frac{l+1}{s} \right) j_l(s)$$

(c) When V_0 is finite (but still large), the value of $\partial \Psi_m / \partial r$ at $r = R_0$ should still be close to what it was for $V_0 = \infty$. Moreover, a good approximation of the wavefunction within the helium ($r > R_0$) is given by

$$\Psi_m(r, \hat{\mathbf{r}}) \approx \Psi_m(R_0, \hat{\mathbf{r}}) e^{-K(r-R_0)} ,$$

where $(\hbar K)^2 / 2m_e = V_0 - E_1$. Combine these two approximations and your result from (b) to obtain

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

(d) You are now ready to calculate the Jahn-Teller effect. Show that the quadrupolar shape deformation $\Delta R(\hat{\mathbf{r}}) = \epsilon P_2(\cos \theta)$ breaks the degeneracy of the p-states to first order in H_{int} . Which state (or linear combination) becomes non-degenerate?

(e) Let $\Delta E_1(\epsilon)$ be the first order energy shift of the non-degenerate state you calculated in (d). What sign of deformation, $\epsilon > 0$ (prolate) or $\epsilon < 0$ (oblate), lowers the energy? Using the bubble parameters from assignment 4 and $V_0 \approx 1\text{eV}$ estimate the magnitude of the generalized force $F = \Delta E_1(\epsilon) / \epsilon$ in units of Newtons.