

Ph135a

**Problem Set #4 (Parts IV.3 and V.1 -- V.2)**

November 15, 2016  
(Due: November 29, 2016)

### 1. Sum rule for oscillator strengths and dielectric constant of a semiconductor

Consider the Hamiltonian for the electrons in a semiconducting crystal,

$$\mathcal{H} = -(\hbar^2/2m)\nabla^2 + \mathcal{V}(\mathbf{r}),$$

where  $\mathcal{V}(\mathbf{r})$  is the potential energy of the crystal.

(a) If  $|\mu\rangle$  and  $|\nu\rangle$  denote the eigenstates for the eigen-energies  $E_\mu$  and  $E_\nu$  of the Hamiltonian  $\mathcal{H}$ , verify the following sum rule for oscillator strengths

$$\sum_{\mu} (E_{\mu} - E_{\nu}) |\langle \mu | e^{i\mathbf{q}\cdot\mathbf{r}} | \nu \rangle|^2 = (\hbar^2 q^2 / 2m) \quad (\text{IV-71})$$

by considering an expansion of the expectation value of the double commutator

$$[[\mathcal{H}, e^{i\mathbf{q}\cdot\mathbf{r}}], e^{-i\mathbf{q}\cdot\mathbf{r}}] \quad (\text{IV-72})$$

in the eigenstate  $|\nu\rangle$ .

(b) Using first-order time-dependent perturbation theory, we find that the dielectric constant of a semiconductor satisfies the following expression:

$$\varepsilon(\mathbf{q}, \omega) = 1 + \frac{4\pi e^2}{q^2} \lim_{\alpha \rightarrow 0^+} \sum_{\mathbf{k}, \mathbf{g}} \frac{|\langle \mathbf{k} | e^{i\mathbf{q}\cdot\mathbf{r}} | \mathbf{k} + \mathbf{q} + \mathbf{g} \rangle|^2}{E(\mathbf{k} + \mathbf{q} + \mathbf{g}) - E(\mathbf{k}) - \hbar\omega + i\hbar\alpha} \{f^0(\mathbf{k}) - f^0(\mathbf{k} + \mathbf{q} + \mathbf{g})\} \quad (\text{IV-69})$$

where  $f^0(\mathbf{k})$  is the Fermi-Dirac function and  $\mathbf{g}$  denotes the reciprocal lattice vectors. Using EQs. (IV-71) and (IV-69), fill in the missing steps in EQ. (IV.77) and show that in the high-frequency limit, the dielectric constant is indeed given by

$$\varepsilon(\mathbf{q}, \omega) = 1 - \frac{4\pi n_e e^2}{m\omega^2} \equiv 1 - \left( \frac{\omega_p^2}{\omega^2} \right), \quad (\text{IV-77})$$

where  $n_e$  denotes the density of electrons in the occupied states.

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### 2. Basis functions and irreducible representations of the $O_h$ group

In the following we define  $R$  as the elements of the group  $G(R)$ ,  $h$  the order of the group,  $D^{(\alpha)}$  an irreducible representation of  $G(R)$  with dimension  $l_{\alpha}$ ,  $\chi^{(\alpha)}(R)$  the character of  $D^{(\alpha)}$ , and the operators  $\hat{O}_R$  that transform functions  $f(\vec{r})$  according to the relation  $\hat{O}_R f(R\vec{r}) = f(\vec{r})$ .

(a) Using the character table of the cubic group  $O_h$  and the projection operators

$$\hat{P}^{(\alpha)} = \frac{l_\alpha}{h} \sum_R \chi^{(\alpha)}(R)^* \hat{O}_R, \quad (\text{V-34})$$

show that the functions  $x$ ,  $y$  and  $z$  are a set of basis functions for the irreducible representation  $\Gamma_{15}$ , and that the functions  $xy$ ,  $yz$  and  $zx$  are a set of basis functions for the irreducible representation  $\Gamma_{25}'$ .

(b) Find all  $(3 \times 3)$  matrices for the representation  $\Gamma_{15}$  by using the basis functions  $x$ ,  $y$  and  $z$ .

(c) Find all  $(3 \times 3)$  matrices for the representation  $\Gamma_{25}'$  by using the basis functions  $xy$ ,  $yz$  and  $zx$ .

### 3. Molecular vibration modes of $\text{XH}_3$

In this problem we consider a fictitious molecule  $\text{XH}_3$  that is the planar version of the ammonia molecule, as illustrated in Fig. P4-1. We want to use this example to help you familiarize the concept of symmetry groups and the phonon modes of a molecule with given symmetry.

(a) Find the symmetry group  $\mathcal{G}$  that leaves  $\text{XH}_3$  invariant under its symmetry operations.

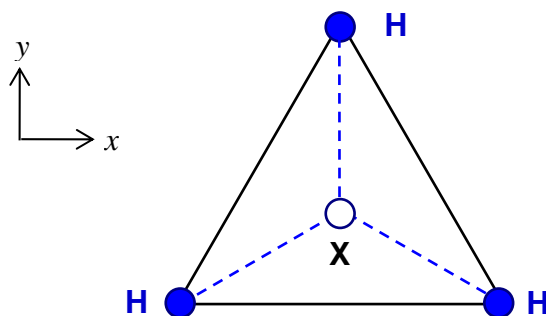
(b) Find the molecular vibrational modes in terms of the irreducible representations of the point group  $\mathcal{G}$  that you have identified in (a).

(c) Identify the Raman-active, infrared-active and silent modes in (b).

(d) Sketch the normal vibrations of atoms for the Raman-active and infrared-active modes.

(e) Suppose that a strain is applied along the  $y$ -axis so that the shape of the molecule is distorted. Find the new the symmetry group  $S$ , which is clearly a subgroup of  $\mathcal{G}$ .

(f) Discuss which originally degenerate phonon modes are now split into new modes.



**Fig. P4-1:** Schematics of the structure of a planar molecule  $\text{XH}_3$  on the  $x$ - $y$  plane.

#### 4. Symmetry reduction from the rotation-inversion group $O(3)$ to the cubic group $O_h$

The spherical harmonics  $Y_{lm}(\theta, \phi)$  ( $m = -l, -l+1, \dots, l-1, l$ ) with even (odd)  $l$  constitute a basis for the irreducible representation  $D^{(l+)} (D^{(l-)})$  of the rotation-inversion group  $O(3)$ . A rotation through an angle  $\alpha$  about the  $z$ -axis is represented by the irreducible representation  $D^{(l)}$  with the character

$$\chi^{(l)}(\alpha) = \frac{\sin[(2l+1)\alpha/2]}{\sin(\alpha/2)}. \quad (\text{V-43})$$

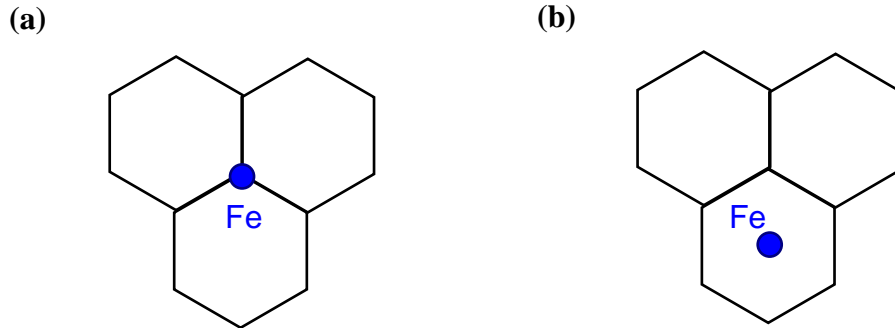
- (a) Consider the states of an atom split by a perturbation with the cubic symmetry  $O_h$ . Show that the irreducible representation of  $O(3)$  with  $l$  up to 3 are decomposed into the following representations of  $O_h$ :

$$\begin{aligned} \text{State } s(l=0) &= \Gamma_1, \\ \text{State } p(l=1) &= \Gamma_{15}, \\ \text{State } d(l=2) &= \Gamma'_{25} + \Gamma_{12}, \\ \text{State } f(l=3) &= \Gamma_{15} + \Gamma_{25} + \Gamma'_2. \end{aligned}$$

- (b) Find the proper linear combinations of spherical harmonics up to  $l=2$  that are basis functions for the irreducible representations of the point group  $O_h$ . [Hint: Use the character table of  $O_h$ , and apply the projection operators to spherical harmonics.]

#### 5. Crystal fields in a two-dimensional honeycomb lattice

In this problem we investigate how the crystal fields of an iron (Fe) impurity may vary in two different locations of a honeycomb lattice. Suppose that a Fe-impurity is introduced into a honeycomb lattice, which is a two-dimensional approximation for a graphite structure. In the first case the Fe-impurity is placed in a *substitutional* location, as shown in Fig. P4-2(a), and in the second case the impurity is placed in an *interstitial* location, as shown in Fig. P4-2(b).



**Fig. P4-2** (a) Substitutional and (b) interstitial locations of an iron impurity in a honeycomb lattice.

- (a) Considering only the nearest neighbors of the Fe-impurity, find the difference in the crystal potential of the *substitutional* location and that of the *interstitial* location.
- (b) For the *substitutional* case, express the crystal field in part (a) in terms of spherical harmonics for the lowest order terms with angular dependence.
- (c) Using the proper point group symmetry and character table, give the crystal field splitting of the five-fold *d*-levels of the Fe-impurity in the crystal fields of part (a).