

The answers of problems in “Raman spectroscopy in Graphene Related Systems”

(August 7, 2012 updated)

Edited by R. Saito

Q:1-1 The carbon-carbon distance of graphene (see Fig. 1.1) is 1.42\AA . How much area is occupied by a single carbon atom in the graphene plane?

Answer: Graphene is a two-dimensional hexagonal lattice. Each hexagonal ring consists of six carbon atoms and each carbon atom is shared by three hexagons. Thus there are two carbon atoms per a hexagonal ring as shown in Fig. (1-1-1).

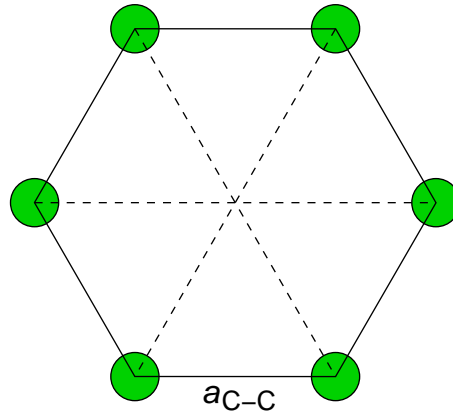


Figure 1-1-1: Each hexagon has 6 carbon atoms and each carbon atom is shared by three hexagon. Thus there are 2 carbon atoms in the hexagon.

The area of the hexagon corresponds to six times of the regular triangle whose edge length is a_{C-C} . Thus the area occupied by a single carbon atom is three times of the triangle which is given by

$$3 \times \frac{\sqrt{3}}{4} a_{C-C}^2 = 2.62\text{\AA}^2 = 2.62 \times 10^{-20} \text{m}^2 \tag{1-1-1}$$

Here we used the value $a_{C-C}=1.42\text{\AA}$ in Eq. (1-1-1).

Riichiro Saito (rsaito@flex.phys.tohoku.ac.jp) (02/14/11)

Q:1-6 Each carbon atom in a C_{60} molecule has one pentagonal and two hexagonal rings. Calculate the angles (a) between the two hexagonal rings and (b) between the hexagonal ring and the pentagonal ring.

(a) See Fig. 1-6-1 . If we apply the law of cosines to the triangles ABC and ADC, with respect to the side AC, we obtain

$$\begin{aligned} d^2 &= 2l^2(1 - \cos(\beta)) \\ d^2 &= 2h^2(1 - \cos(\alpha)) \end{aligned} \tag{1-6-1}$$

For the case of fullerene, the parameters in the figure are adapted in the following manner: β is the angle of the pentagon, $\beta = 3\pi/5$; l is the side of the hexagon/pentagon, and the planes depicted are the hexagon planes. We may, for convenience, define $l = 2R$. Since h is at right angles to the axis that intersect the two hexagon planes, h is the hexagon height, $h = \sqrt{3}l/2 = \sqrt{3}R$.

Therefore, the Eq. 1-6-1 yields

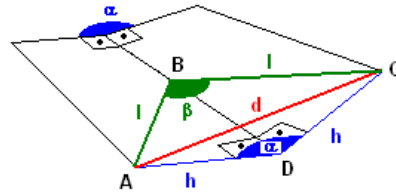


Figure 1-6-1: Auxiliary geometric construction to help determining α , the angle between the two hexagon sheets.

$$\alpha = \cos^{-1}[3 - 4(1 - \cos(3\pi/5))]/3 \approx 139^\circ. \tag{1-6-2}$$

(b) See Fig. 1-6-2. The angle we wish to calculate is γ .

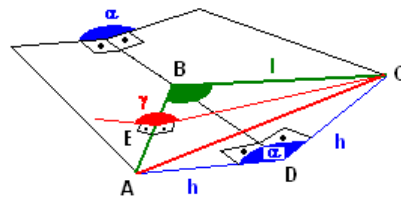


Figure 1-6-2: γ is the angle between the pentagon and the hexagon planes.

Let us now consider the ABCD prism in Fig. 1-6-3.

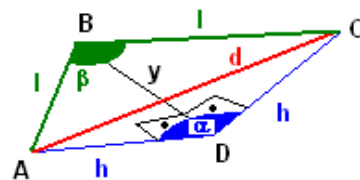


Figure 1-6-3: Focused view of prism ABCD from Fig.1-6-2

We may construct two perpendicular segments forming an angle γ' : the first one is the height of the triangle ABC with respect to the side AB. Let us call it CE (see Fig. 1-6-2). The other one is constructed in the following manner: trace a segment perpendicular to AB, starting from point E, in the plane ABD, which intersects the straight line AD on the point P. That is segment the segment EP. Fig. 1-6-4 shows EP in the plane of the triangle ABD. We shall thus define γ' , by this construction, as the angle between CE and EP.

As it was meant to be, $\gamma' = \pi - \gamma$. Let us now consider the triangle EPC as in Fig 1-6-5.

Let us call u the magnitude of the segment EC and x the magnitude of the segment EP. We note that

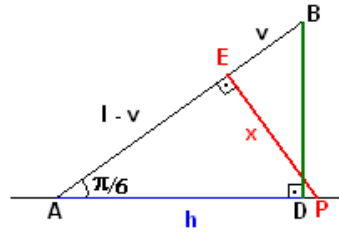


Figure 1-6-4: EP segment on the ABD triangle’s plane.

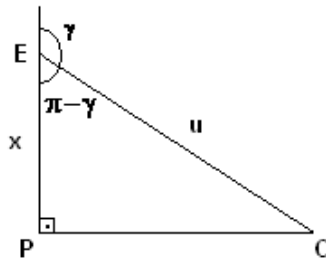


Figure 1-6-5: Triangle EPC.

since the planes of the triangles ABD and ADC are perpendicular, (see Fig. 1-6-3), trigonometry on a rectangle triangle yields

$$\cos(\gamma') = -\cos(\gamma) = x/u \tag{1-6-3}$$

In terms of the known parameters, who are x and u ? Fig. 1-6-2 shows that $u = l \sin(\beta)$. If we define $v = l \cos(\beta)$, the magnitude of the segment BE, then Fig. 1-6-4 shows us that $x = (l - v) \tan(\pi/6)$. Therefore, using that $\beta = 3\pi/5$, we have

$$\gamma = \cos^{-1}[\sqrt{3}(\cos(\beta) - 1)/3 \sin(\beta)] \approx 143^\circ. \tag{1-6-4}$$

Answer:

Lucas Mussnich (mussnich@ufmg.br) (03/14/11)

Q:1-8 In spectroscopy, a wave vector is defined by $1/\lambda$ (where λ is the wavelength) while in solid state physics, the definition of a wave vector is $2\pi/\lambda$. Show that a 1eV photon corresponds to 8065 cm^{-1} (wavenumber). In Raman spectroscopy, the difference between the wave vectors for the incident and scattered light is called the Raman shift whose units are generally given in cm^{-1} .

Answer: The Energy of a photon is given by

$$E = \hbar c \frac{2\pi}{\lambda}, \tag{1-8-1}$$

where $\hbar = (1.054571596 \pm 0.000000082) \times 10^{-34}$ J·s is the Planck constant and $c = 2.99792458 \times 10^{10}$ cm·s⁻¹ is the velocity of light. Using Eq. (1-8-1), we can obtain the corresponding value of the wave vector for a $1eV = (1.602176462 \pm 0.000000063) \times 10^{-19}$ J photon in the units of cm⁻¹ as follows:

$$\begin{aligned} \frac{1}{\lambda} &= \frac{1}{2\pi} \frac{E}{\hbar c} \\ &= \frac{1}{2\pi} \frac{(1.602176462 \pm 0.000000063) \times 10^{-19} \text{ J}}{(1.054571596 \pm 0.000000082) \times 10^{-34} \text{ J} \cdot \text{s} \times 2.99792458 \times 10^{10} \text{ cm} \cdot \text{s}^{-1}} \\ &= 8065.54477 \pm 0.00094 \text{ cm}^{-1}. \end{aligned} \quad (1-8-2)$$

Shoichi Takahata (physics2070@yahoo.co.jp) (02/03/12)

Q:1-10 Consider the optical electric field of the incident light with an angular frequency $\omega_0 = 2\pi\nu_0$ and amplitude E_0 ,

$$E = E_0 \cos \omega_0 t.$$

Then the dipole moment P of a diatomic molecule is proportional to E such that $P = \alpha E$, in which α is called the polarizability. When the molecule is vibrating with a frequency ω , then α is also vibrating with the frequency ω ,

$$\alpha = \alpha_0 + \alpha_1 \cos \omega t.$$

When substituting α into the formula $P = \alpha E$, show that there are three different frequencies for the scattered light (or P), ω_0 (elastic, Rayleigh scattering) and $\omega_0 \pm \omega$ (inelastic, Stokes (-) and anti-Stokes (+) Raman scattering).

Answer: The incoming electric field varies sinusoidally as

$$E = E_0 \cos 2\pi\nu_0 t \quad (1-10-1)$$

where E_0 is the amplitude and ν_0 is the frequency of the laser. For a diatomic molecule the induced dipole moment P is

$$P = \alpha E = \alpha E_0 \cos 2\pi\nu_0 t \quad (1-10-2)$$

α is the polarizability. The vibration of the molecule is also sinusoidal, with frequency ν_m , and described by the nuclear displacement coordinate q ,

$$q = q_0 \cos 2\pi\nu_m t \quad (1-10-3)$$

where q_0 is the amplitude. If the amplitude is small, α can be expanded as a function of the coordinate q as,

$$\alpha = \alpha_0 + \left(\frac{\partial \alpha}{\partial q} \right)_0 q + \dots \quad (1-10-4)$$

where α_0 is the polarizability at the equilibrium position, and $\left(\frac{\partial \alpha}{\partial q} \right)_0$ is the rate of change of α with respect to the change in the coordinate q evaluated at the equilibrium position. Combining the expressions for P , q , and α yields,

$$P = \alpha E_0 \cos 2\pi\nu_0 t = \left(\alpha_0 + \left(\frac{\partial \alpha}{\partial q} \right)_0 q \right) E_0 \cos 2\pi\nu_0 t \quad (1-10-5)$$

$$P = \alpha_0 E_0 \cos 2\pi\nu_0 t + \left(\frac{\partial \alpha}{\partial q} \right)_0 q E_0 \cos 2\pi\nu_0 t \quad (1-10-6)$$

$$P = \alpha_0 E_0 \cos 2\pi\nu_0 t + \left(\frac{\partial \alpha}{\partial q} \right)_0 q_0 E_0 \cos 2\pi\nu_m t \cos 2\pi\nu_0 t \quad (1-10-7)$$

$$P = \alpha_0 E_0 \cos 2\pi\nu_0 t + \frac{1}{2} \left(\frac{\partial \alpha}{\partial q} \right)_0 q_0 E_0 \left[\cos 2\pi(\nu_0 + \nu_m) t + \cos 2\pi(\nu_0 - \nu_m) t \right] \quad (1-10-8)$$

The first term in Eq. (1-10-8) represents the Rayleigh scattered light with the same frequency as that of the incident laser light, the second term represents the anti-Stokes shifted light with frequency $(\nu_0 + \nu_m)$, and the last term represents the Stokes shifted light with a frequency of $(\nu_0 - \nu_m)$.

Daniel Casimir (casimir.daniel@gmail.com) (08/03/12)

Q:2-3 Plot the rough shape of R_{nl} in Eq. (2.2) for 1s, 2s and 2p states as a function of r . Explain how these functions are orthogonal to each other.

Answer: We consider a hydrogen atom. From Eq. (2.6) in the book, the form of $R_{nl}(r)$ for an electron of a hydrogen atom ($Z = 1$) is expressed by

$$R_{nl}(r) = C_{nl} \exp\left(-\frac{r}{na_0}\right) \left(\frac{r}{a_0}\right)^l G_{nl}\left(\frac{r}{a_0}\right), \quad (2-3-1)$$

where C_{nl} denotes the normalization constant. G_{nl} denotes the Laguerre polynomials as a function of $\rho = r/a_0$ (where a_0 is the Bohr radius, $a_0 = \hbar^2/me^2$) and is defined by

$$G_{nl}(\rho) = L_{n+l}^{2l+1}\left(\frac{2\rho}{n}\right) = \frac{d^{2l+1}}{dx^{2l+1}} \left(\exp(x) \frac{d^{n+l}}{dx^{n+l}} x^{n+l} \exp(-x) \right) \Big|_{x=\frac{2\rho}{n}}. \quad (2-3-2)$$

Since $(n, l) = (1, 0)$, $(2, 0)$, and $(2, 1)$ correspond to 1s, 2s and 2p states, respectively, normalized R_{nl} of Eq. (2-3-1) for 1s, 2s and 2p states as a function of r/a_0 can be written as follows:

$$R_{10}(r) = C_{10} \exp\left(-\frac{r}{a_0}\right), \quad (2-3-3)$$

$$R_{20}(r) = C_{20} \left(1 - \frac{r}{2a_0}\right) \exp\left(-\frac{r}{2a_0}\right), \quad (2-3-4)$$

$$R_{21}(r) = C_{21} \left(\frac{r}{a_0}\right) \exp\left(-\frac{r}{2a_0}\right), \quad (2-3-5)$$

where the normalization constants are given by $C_{10} = 2a_0^{-3/2}$, $C_{20} = a_0^{-3/2}/\sqrt{2}$, and $C_{21} = a_0^{-3/2}/2\sqrt{6}$, which can be obtained by the normalization condition as:

$$\int_0^\infty dr r^2 R_{nl}(r)^* R_{nl}(r) = 1. \quad (2-3-6)$$

In Fig. 2-3-1, we plot R_{nl}/C_{nl} for 1s, 2s, and 2p orbital as a function of r/a_0 . The inner product of radial wave functions $I_{nl'n'l'}$ of Eqs. (2-3-3), (2-3-4) and (2-3-5) is given by

$$I_{nl'n'l'} = \int_0^\infty dr r^2 R_{nl}(r)^* R_{n'l'}(r). \quad (2-3-7)$$

Using the formula

$$\int_0^\infty dr r^m \exp(-\alpha r) = m! \alpha^{-(m+1)}, \quad (2-3-8)$$

where α is a positive constant and m is non-negative integer, we can calculate Eq. (2-3-7) as follows:

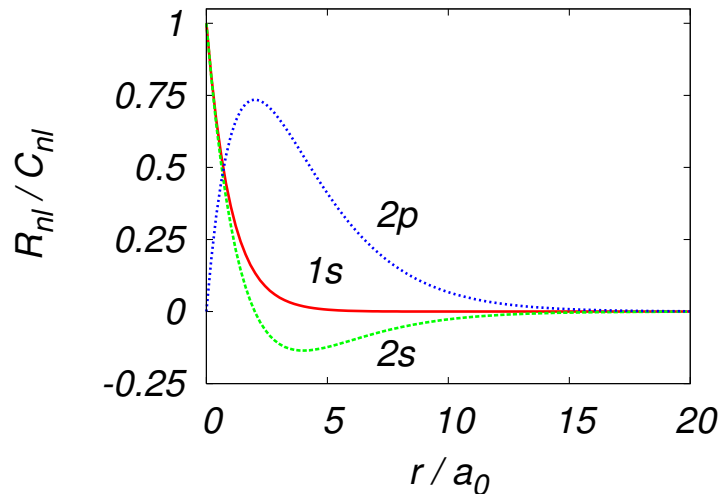


Figure 2-3-1: The radial wave functions of a hydrogen atom for 1s, 2s and 2p orbitals.

$$\begin{aligned}
 I_{1020} &= \int_0^{\infty} dr r^2 R_{10}(r) R_{20}(r) \\
 &= \frac{\sqrt{2}}{a_0^3} \int_0^{\infty} dr r^2 \exp\left(-\frac{3r}{2a_0}\right) - \frac{\sqrt{2}}{a_0^3} \frac{1}{2a_0} \int_0^{\infty} dr r^3 \exp\left(-\frac{3r}{2a_0}\right) \\
 &= \frac{16\sqrt{2}}{27} - \frac{\sqrt{2}}{2} \frac{32}{27} \\
 &= 0,
 \end{aligned} \tag{2-3-9}$$

$$\begin{aligned}
 I_{1021} &= \int_0^{\infty} dr r^2 R_{10}(r) R_{21}(r) \\
 &= \frac{1}{\sqrt{6}a_0^3} \frac{1}{a_0} \int_0^{\infty} dr r^3 \exp\left(-\frac{3r}{2a_0}\right) \\
 &= \frac{32}{27\sqrt{6}} \\
 &\neq 0,
 \end{aligned} \tag{2-3-10}$$

$$\begin{aligned}
 I_{2021} &= \int_0^{\infty} dr r^2 R_{20}(r) R_{21}(r) \\
 &= \frac{1}{4\sqrt{3}a_0^3} \frac{1}{a_0} \int_0^{\infty} dr r^3 \exp\left(-\frac{r}{a_0}\right) - \frac{1}{4\sqrt{3}a_0^3} \frac{1}{2a_0^2} \int_0^{\infty} dr r^4 \exp\left(-\frac{r}{a_0}\right) \\
 &= \frac{6}{4\sqrt{3}} - \frac{12}{4\sqrt{3}} \\
 &= -\frac{6}{4\sqrt{3}} \\
 &\neq 0,
 \end{aligned} \tag{2-3-11}$$

which show that radial wave functions for only 1s and 2s states are orthogonal to each other. For 1s and 2p (2s and 2p) orbitals, the orthogonal condition is satisfied by the orthogonality of spherical harmonics Y_{lm} .

Shoichi Takahata (physics2070@yahoo.co.jp) (02/03/12)

Q:2-6 Using the unitary matrix U in Eq. (2.16), diagonalize the Hamiltonian in Eq. (2.14).

Answer: The diagonalization can be done by a unitary transformation of the Hamiltonian matrix H given by $U^\dagger H U$, where the Hamiltonian H and the unitary matrix U are given, respectively, by Eqs. (2.13) and (2.15):

$$\begin{aligned}
 U^\dagger H U &= \frac{1}{2} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \begin{pmatrix} E_{1s} & V_0 \\ E_{1s} & V_0 \end{pmatrix} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \\
 &= \frac{1}{2} \begin{pmatrix} E_{1s} + V_0 & V_0 + E_{1s} \\ E_{1s} - V_0 & V_0 - E_{1s} \end{pmatrix} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \\
 &= \frac{1}{2} \begin{pmatrix} 2(E_{1s} + V_0) & 0 \\ 0 & 2(E_{1s} - V_0) \end{pmatrix} \\
 &= \begin{pmatrix} E_{1s} + V_0 & 0 \\ 0 & E_{1s} - V_0 \end{pmatrix} \tag{2-6-1}
 \end{aligned}$$

Shotaro Maruyama (shotaro.maruyama@cmpt.phys.tohoku.ac.jp) (2/3/12)

Q:2-7 Solve the Schrödinger equation for the H molecule for the case that $s = \langle \Psi_1 | \Psi_2 \rangle$ is not zero. Obtain both eigenvalues and wave functions.

Answer:

We consider the Hamiltonian $H = H_0 + V$ where H_0 and V mean, respectively, unperturbed Hamiltonian of isolated H atoms and interactions between one hydrogen atom and another hydrogen atom. H_0 satisfy the following equation.

$$H_0 |\Psi_i\rangle = E_s |\Psi_i\rangle \quad (i = 1, 2), \tag{2-7-1}$$

where E_s and $|\Psi_i\rangle$ are eigenvalue and eigen vector of each H atom, respectively. We express the eigenstate of the molecule by taking linear combination of atomic orbitals as follows:

$$|\Psi\rangle = C_1 |\Psi_1\rangle + C_2 |\Psi_2\rangle, \tag{2-7-2}$$

where C_1 and C_2 are coefficients to be solved. The Schrödinger equation $H|\Psi\rangle = E|\Psi\rangle$ gives

$$C_1 H |\Psi_1\rangle + C_2 H |\Psi_2\rangle = E(C_1 |\Psi_1\rangle + C_2 |\Psi_2\rangle). \tag{2-7-3}$$

Operating $\langle \Psi_1 |$ from left side in Eq. (2-7-3), we get

$$\begin{aligned}
 C_1 E'_s + C_2 E_s S + C_2 V_0 &= C_1 E + C_2 E S \\
 (E'_s - E)C_1 + (E_s S + V_0 - E S)C_2 &= 0, \tag{2-7-4}
 \end{aligned}$$

where $E'_s = \langle \Psi_i | H | \Psi_i \rangle$, $V_0 = \langle \Psi_1 | V | \Psi_2 \rangle = \langle \Psi_2 | V | \Psi_1 \rangle$, and $S = \langle \Psi_1 | \Psi_2 \rangle = \langle \Psi_2 | \Psi_1 \rangle$. Similarly, we get the following equation by operating $\langle \Psi_2 |$ from left side in Eq. (2-7-3):

$$(E_s S + V_0 - E S)C_1 + (E'_s - E)C_2 = 0. \tag{2-7-5}$$

In matrix form, Eqs. (2-7-5) and (2-7-6) can be written as:

$$\begin{pmatrix} E_s - E & \epsilon - E S \\ \epsilon - E S & E'_s - E \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}, \tag{2-7-6}$$

where $\epsilon = E_s S + V_0$. In order to get not trivial solution for $\begin{pmatrix} C_1 \\ C_2 \end{pmatrix}$, we get the following secular equation.

$$\det \begin{pmatrix} E'_s - E & \epsilon - E S \\ \epsilon - E S & E'_s - E \end{pmatrix} = 0. \tag{2-7-7}$$

We obtain E by using Eq. (2-7-7) as follows:

$$\begin{aligned} (E'_s - E)^2 - (\epsilon - ES)^2 &= 0 \\ (1 - S^2)E^2 + 2(\epsilon - E'_s)E + E'^2_s - \epsilon^2 &= 0 \\ (1 - S^2) \left\{ E - \frac{E'_s + \epsilon}{1 + S} \right\} \left\{ E - \frac{E'_s - \epsilon}{1 - S} \right\} &= 0, \end{aligned}$$

which gives

$$E_{\pm} = \frac{E'_s \pm \epsilon}{1 \pm S}. \quad (2-7-8)$$

In the case of $E = E_+$, Eq. (2-7-6) is written as:

$$\begin{pmatrix} E'_s - E_+ & \epsilon - E_+S \\ \epsilon - E_+S & E'_s - E_+ \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}. \quad (2-7-9)$$

Eq. (2-7-9) gives

$$C_1 : C_2 = \epsilon - E_+S : E_+ - E'_s = 1 : 1. \quad (2-7-10)$$

Normalizing $|\Psi\rangle$, we determine the coefficients of Eq. (2-7-2) as follows:

$$\begin{aligned} 1 = \langle \Psi | \Psi \rangle &= |C_1|^2 (\langle \Psi_1 | \Psi_1 \rangle + \langle \Psi_1 | \Psi_2 \rangle + \langle \Psi_2 | \Psi_1 \rangle + \langle \Psi_2 | \Psi_2 \rangle) \\ &= 2|C_1|^2(1 + S). \end{aligned} \quad (2-7-11)$$

Using Eq. (2-7-11), C_1 and C_2 are written as:

$$C_1 = C_2 = \frac{1}{\sqrt{2(1 + S)}}. \quad (2-7-12)$$

Thus we get the eigenstate of the molecule:

$$|\Psi_+\rangle = \frac{1}{\sqrt{2(1 + S)}} (|\Psi_1\rangle + |\Psi_2\rangle). \quad (2-7-13)$$

Similarly, we get the eigenstate of the molecule for the case of $E = E_-$ as follows:

$$|\Psi_-\rangle = \frac{1}{\sqrt{2(1 - S)}} (|\Psi_1\rangle - |\Psi_2\rangle). \quad (2-7-14)$$

$|\Psi_+\rangle$ and $|\Psi_-\rangle$ are, respectively, bonding and anti-bonding states.

Shotaro Maruyama (shotaro.maruyama@cmpt.phys.tohoku.ac.jp) (2/3/12)

Q:2-10 Obtain Eqs.(2.33) and (2.34). Evaluate the value of the Fermi velocity.

Answer: Using the phase factor $f(k)$ in Eq. (2.28);

$$f(k) = 1 + 4 \cos\left(\frac{\sqrt{3}k_x a}{2}\right) \cos\left(\frac{k_y a}{2}\right) + 4 \cos^2\left(\frac{k_y a}{2}\right), \quad (2-10-1)$$

The electronic energy $E^{\pm}(k_x, k_y)$ of graphene is given by Eq. (2.32);

$$\begin{aligned} E^{\pm}(k_x, k_y) &= \pm t \sqrt{|f(k)|^2} \\ &= \pm t \sqrt{1 + 4 \cos\left(\frac{\sqrt{3}k_x a}{2}\right) \cos\left(\frac{k_y a}{2}\right) + 4 \cos^2\left(\frac{k_y a}{2}\right)}, \end{aligned} \quad (2-10-2)$$

where t is the nearest neighbor transfer integral which is also called $-\gamma_0$ ($t = -\gamma_0$). γ_0 is given a positive value. We can evaluate the Fermi velocity as follows. At first, we calculate the lowest order term in $f(k)$ around the K points. Because the K point has a three-fold rotational symmetry in the k -space, the first order term in $f(k)$ becomes zero. For example, when we consider a K point;

$$K = \left(0, -\frac{4\pi}{3a}\right), \quad (2-10-3)$$

the lowest order term in $f(k)$ is written as

$$\begin{aligned} \left. \frac{\partial f(k)}{\partial k_x} \right|_{k_x=0} &= 0 \\ \left. \frac{\partial f(k)}{\partial k_y} \right|_{k_y=\frac{4\pi}{3a}} &= 0. \end{aligned} \quad (2-10-4)$$

Thus the $f(k)$ is written as

$$\begin{aligned} f(k) &= f(k)|_{k_x=0, k_y=-\frac{4\pi}{3a}} + \left. \frac{\partial^2 f(k)}{\partial k_x^2} \right|_{k_x=0} + \left. \frac{\partial^2 f(k)}{\partial k_y^2} \right|_{k_y=-\frac{4\pi}{3a}} + 2 \left. \frac{\partial^2 f(k)}{\partial k_x \partial k_y} \right|_{k_x=0, k_y=-\frac{4\pi}{3a}} \\ &= \frac{3a^2 k^2}{4}, \end{aligned} \quad (2-10-5)$$

where k^2 is defined by $k^2 = k_x^2 + k_y^2$. If we use the definition of the Fermi velocity;

$$v_F = \left. \frac{1}{\hbar} \frac{\partial E}{\partial k} \right|_{E=E_F}, \quad (2-10-6)$$

The $E^\pm(k)$ can expressed by

$$E^\pm(k) = \pm \hbar v_F |k|. \quad (2-10-7)$$

Using Eqs. (2-10-2) and (2-10-5), we got Fermi velocity as follows;

$$v_F = \sqrt{3} \left(\frac{\gamma_0 a}{2} \hbar \right), \quad (2-10-8)$$

Kouki Yonaga (yona@cmpt.phys.tohoku.ac.jp) (12/7/11)

Q:2-12 Plot the density of states for the parabolic energy band, $E = a(k_x^2 + k_y^2)$.

Answer: We now consider the parabolic energy band in two dimension as follows:

$$E = a(k_x^2 + k_y^2) = ak^2, \quad (2-12-1)$$

where k is $\sqrt{k_x^2 + k_y^2}$. If the length of x and y axis in the system is L_x and L_y , the area which a microscopic state occupies in the reciprocal space is $\frac{2\pi}{L_x} \cdot \frac{2\pi}{L_y}$. When we consider the isotropic two dimensional plane in k space, the number of states dN with the wave number from k to $k + dk$ is written as:

$$dN = 2 \cdot \frac{2\pi k dk}{\frac{2\pi}{L_x} \cdot \frac{2\pi}{L_y}} = \frac{Sk}{\pi} dk, \quad (2-12-2)$$

where the factor 2 is the spin degeneracy and $S = L_x \cdot L_y$ is the area of the system. Using Eq. (2-12-2), we obtain

$$\frac{dN}{dk} = \frac{Sk}{\pi}. \quad (2-12-3)$$

Using Eq. (2-12-1), we obtain

$$\frac{dE}{dk} = 2ka. \quad (2-12-4)$$

Using Eqs. (2-12-3) and (2-12-4), we can obtain the density of states for the parabolic energy band $E = a(k_x^2 + k_y^2)$ as follows:

$$D(E) = \frac{dN}{dE} = \frac{\frac{dN}{dk}}{\frac{dE}{dk}} = \frac{S}{2\pi a}. \quad (2-12-5)$$

In Fig. (2-12-1), the density of states for the parabolic energy band is plotted as a function of the energy E .

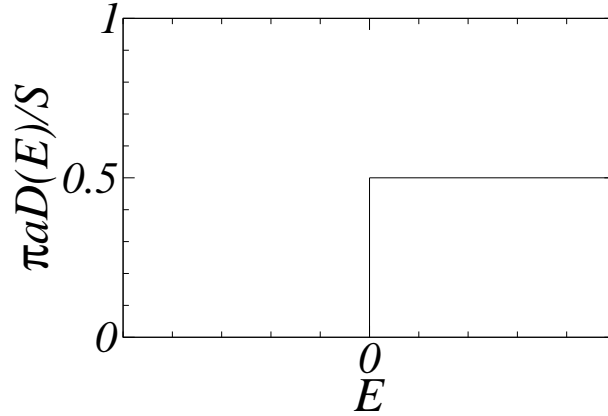


Figure 2-12-1: Density of states (DOS) for the parabolic energy band $E = a(k_x^2 + k_y^2)$. The DOS is constant for $E > 0$.

Yuki Tatsumi (tatsumi@flex.phys.tohoku.ac.jp) (02/05/12)

Q:2-13 By expanding $f(k)$ of Eq. (2.28) near the K point, show that the Hamiltonian matrix is written by Eq. (2.35).

Answer: We use the definition of the real space unit vectors \mathbf{a}_1 and \mathbf{a}_2 and the reciprocal space unit vectors \mathbf{b}_1 and \mathbf{b}_2 , shown in Fig. (2-13-1). This definition is the same as the textbook.

Using the definition, the sum of the phase factors $f(k)$ (Eq. (2.28) in the textbook) is given by

$$f(k) = e^{ik_x a/\sqrt{3}} + 2e^{-ik_x a/2\sqrt{3}} \cos\left(\frac{k_y}{2}a\right). \quad (2-13-1)$$

By expanding $f(k)$ around the K point $(0, -4\pi/3a)$,

$$\begin{aligned} f\left(k_x = 0, k_y = -\frac{4\pi}{3a}\right) &= 1 + 2\cos\left(-\frac{2}{3}\pi\right) \\ &= 1 + 2 \cdot \left(-\frac{1}{2}\right) \\ &= 0, \end{aligned} \quad (2-13-2)$$

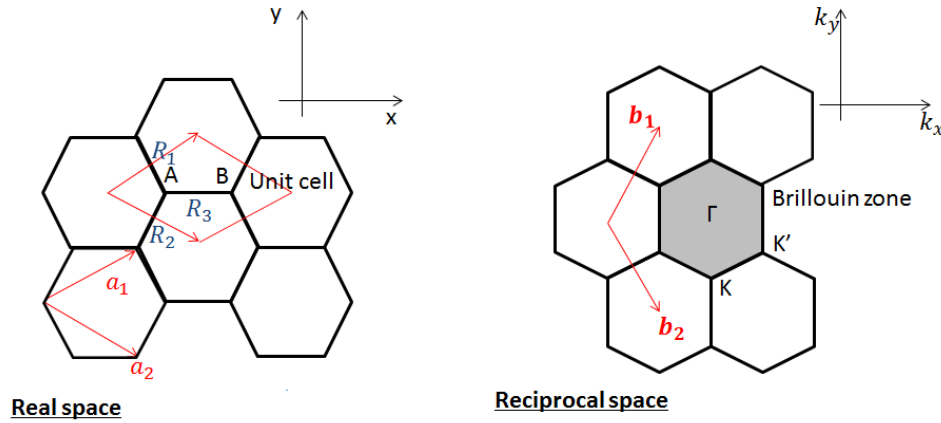


Figure 2-13-1: Definition of the real space unit vectors \mathbf{a}_1 and \mathbf{a}_2 , and the reciprocal space unit vectors \mathbf{b}_1 and \mathbf{b}_2 . The gray zone of the reciprocal space is the first Brillouin zone.

$$\begin{aligned}
 \frac{\partial f}{\partial k_x} \left(k_x = 0, k_y = -\frac{4\pi}{3a} \right) &= \frac{ia}{\sqrt{3}} \cdot e^{ik_x a/\sqrt{3}} - 2 \cdot \frac{ia}{2\sqrt{3}} \cdot e^{-ik_x a/2\sqrt{3}} \cos \left(-\frac{2}{3}\pi \right) \Big|_{k_x=0, k_y=-\frac{4\pi}{3a}} \\
 &= \frac{ia}{\sqrt{3}} - \frac{ia}{\sqrt{3}} \cdot \left(-\frac{1}{2} \right) \\
 &= \frac{\sqrt{3}}{2} ai,
 \end{aligned} \tag{2-13-3}$$

$$\begin{aligned}
 \frac{\partial f}{\partial k_y} \left(k_x = 0, k_y = -\frac{4\pi}{3a} \right) &= 2 \cdot e^{-ik_x a/2\sqrt{3}} \cdot \frac{a}{2} \left\{ -\sin \left(-\frac{2}{3}\pi \right) \right\} \Big|_{k_x=0, k_y=-\frac{4\pi}{3a}} \\
 &= 2 \cdot \frac{a}{2} \cdot \frac{\sqrt{3}}{2} \\
 &= \frac{\sqrt{3}}{2} a,
 \end{aligned} \tag{2-13-4}$$

we can write $f(k)$ as follows:

$$\begin{aligned}
 f(k) &= \frac{\sqrt{3}}{2} aik_x + \frac{\sqrt{3}}{2} a \left(k_y + \frac{4\pi}{3a} \right) \\
 &= \frac{\sqrt{3}}{2} a (ik'_x + ik'_y),
 \end{aligned} \tag{2-13-5}$$

where $k_x = k'_x$, $k_y + \frac{4\pi}{3a} = k'_y$. Using $f(k)$, the Hamiltonian matrix ($\varepsilon_{2p} = 0$) is described by

$$\begin{aligned}
 H &= \begin{pmatrix} \varepsilon_{2p} & tf(k) \\ tf(k)^* & \varepsilon_{2p} \end{pmatrix} \\
 &= -\frac{\sqrt{3}}{2} at \begin{pmatrix} 0 & -ik'_x - k'_y \\ ik'_x - k'_y & 0 \end{pmatrix}
 \end{aligned}$$

$$\begin{aligned}
&= \frac{\sqrt{3}}{2} a \gamma_0 \left[\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} k'_x - \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} k'_y \right] \\
&= \hbar v_F [\sigma_y k'_x - \sigma_x k'_y],
\end{aligned} \tag{2-13-6}$$

where the Fermi velocity $v_F = \frac{\sqrt{3}}{2\hbar} a \gamma_0$, transfer integral $t = -\gamma_0$ and the σ_x and σ_y are the Pauli matrices. To obtain the Hamiltonian of plain formula, we change of the coordinates. It must be that the eigenvalues are invariant when the coordinates are changed. Then we change of the coordinate k'_x and k'_y by rotating by $\pi/2$. The $\pi/2$ rotation matrix is given by

$$C_{\frac{\pi}{2}} = \begin{pmatrix} \cos \frac{\pi}{2} & -\sin \frac{\pi}{2} \\ \sin \frac{\pi}{2} & \cos \frac{\pi}{2} \end{pmatrix} = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}. \tag{2-13-7}$$

Using Eq. (2-13-7), k''_x and k''_y which rotate $\pi/2$ from k'_x and k'_y are given by

$$\begin{aligned}
\begin{pmatrix} k''_x \\ k''_y \end{pmatrix} &= \begin{pmatrix} \cos \frac{\pi}{2} & -\sin \frac{\pi}{2} \\ \sin \frac{\pi}{2} & \cos \frac{\pi}{2} \end{pmatrix} \begin{pmatrix} k'_x \\ k'_y \end{pmatrix} \\
&= \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} k'_x \\ k'_y \end{pmatrix} \\
&= \begin{pmatrix} -k'_y \\ k'_x \end{pmatrix}.
\end{aligned} \tag{2-13-8}$$

Using Eq. (2-13-8), we can obtain

$$k'_x = k''_y, k'_y = -k''_x. \tag{2-13-9}$$

Therefore we can exchange k'_x and k'_y for k''_x and k''_y . Hamiltonian matrix in Eq. (2-13-6) is described by

$$\begin{aligned}
H &= \hbar v_F [\sigma_y k'_x - \sigma_x k'_y] \\
&= \hbar v_F [\sigma_x k''_x + \sigma_y k''_y] \\
&= \hbar v_F (\sigma \cdot \kappa),
\end{aligned} \tag{2-13-10}$$

where $\kappa = -i\nabla$. This is a form of Dirac Hamiltonian. In general, the part of Pauli matrices in the Dirac Hamiltonian have arbitrary property if they satisfy any conditions. These descriptions have the same eigenvalues respectively. Thus we can obtain the same eigenvalues from Eq. (2-13-6) and Eq. (2-13-10) and we can alter Eq. (2-13-6) to the massless Dirac Hamiltonian in Eq. (2-13-10).

Yuki Tatsumi (tatsumi@flex.phys.tohoku.ac.jp) (01/05/12)

Q:2-15 Calculate the diameter for an (n,m) SWNT. What are the values of the diameters for (5,5), (9,0), (10,5) SWNTs? What are possible (n,m) values for SWNTs having a 1.5 ± 0.02 nm diameter?

Answer: A. Calculate the diameter for an (n,m) SWNT.

B. What are the values of diameters for (5,5), (9,0), (10,5) SWNTs?

C. What are possible (n,m) values for SWNTs having a 1.5 ± 0.02 nm?

The parameters

$a = 0.246$ nm : Graphene lattice constant

$\mathbf{a}_1 = \left(\frac{\sqrt{3}}{2}, \frac{1}{2}\right)a$, $\mathbf{a}_2 = \left(\frac{\sqrt{3}}{2}, -\frac{1}{2}\right)a$: Graphene unit vectors

(n, m) : integers such that $0 \leq m \leq n$

$\mathbf{C}_h = n\mathbf{a}_1 + m\mathbf{a}_2$: Nanotube chiral vector

The answer for A

The diameter of a nanotube d_t can be calculated by $|\mathbf{C}_h|/\pi$ whose formula is given as follows:

$$d_t = \frac{a\sqrt{n^2 + nm + m^2}}{\pi} \quad \text{units : nm.} \quad (2-15-1)$$

The answer for B

Substituting $a = 0.246$ nm and each (n, m) value into Eq. (2-15-1), we can obtain the corresponding values of d_t as follows:

$$d_t = \begin{cases} 0.678 \text{ nm} & (n, m) = (5, 5) \\ 0.705 \text{ nm} & (n, m) = (9, 0) \\ 1.04 \text{ nm} & (n, m) = (10, 5) \end{cases} . \quad (2-15-2)$$

The answer for C

From Eq. (2-15-1) and the condition that $1.48 \leq d_t \leq 1.52$, we can obtain the following inequality:

$$\left(\frac{1.48 \times \pi}{0.246}\right)^2 \leq n^2 + nm + m^2 \leq \left(\frac{1.52 \times \pi}{0.246}\right)^2 . \quad (2-15-3)$$

Since $\{(1.48 \times \pi)/0.246\}^2 = 357.2$, $\{(1.52 \times \pi)/0.246\}^2 = 376.8$ and $n^2 + nm + m^2$ is integer, (n, m) values for SWNTs having a 1.5 ± 0.02 nm diameter should satisfy the condition as follows:

$$358 \leq n^2 + nm + m^2 \leq 376 \quad \text{and} \quad 0 \leq m \leq n , \quad (2-15-4)$$

by which we can obtain the proper (n, m) values as follows:

$$(n, m) = (19, 0), (18, 2), (17, 4), (16, 5), (14, 8), (13, 9), (12, 10), (11, 11) . \quad (2-15-5)$$

Shoichi Takahata (physics2070@yahoo.co.jp) (02/03/12)

Q:2-16 For a given (n, m) SWNT, show the expression of $\vec{T} = (t_1, t_2)$ as a function of n and m . What is the length of \vec{T} ?

Answer: If we apply the condition that

$$\vec{T} \cdot \vec{C}_h = 0, \quad (2-16-1)$$

we get

$$(t_1\vec{a}_1 + t_2\vec{a}_2) \cdot (n\vec{a}_1 + m\vec{a}_2) = 0, \quad (2-16-2)$$

where $\vec{a}_1 = \left(\frac{\sqrt{3}}{2}, \frac{1}{2}\right)a$ and $\vec{a}_2 = \left(\frac{\sqrt{3}}{2}, -\frac{1}{2}\right)a$. Eq. (2-16-2) can be expressed by

$$(m + 2n)t_1 + (n + 2m)t_2 = 0. \quad (2-16-3)$$

Thus we get

$$t_1 : t_2 = (n + 2m) : -(m + 2n). \quad (2-16-4)$$

The condition that $\text{gcm}(t_1, t_2) = 1$ gives

$$\begin{aligned} t_1 &= \frac{n + 2m}{d_R}, \\ t_2 &= \frac{m + 2n}{d_R}, \end{aligned} \quad (2-16-5)$$

where $d_R = \text{gcm}(n + 2m, m + 2n)$. The length of \vec{T} is given by using the formula $|\vec{C}_h| = a\sqrt{n^2 + m^2 + nm}$:

$$\begin{aligned} T &= |\vec{T}| \\ &= \sqrt{t_1^2 a^2 + t_2^2 a^2 + t_1 t_2 a^2} \\ &= \frac{a}{d_R} \sqrt{(n + 2m)^2 + (m + 2n)^2 - (n + 2m)(m + 2n)} \\ &= \frac{a}{d_R} \sqrt{3(n^2 + m^2 + nm)} \\ &= \frac{\sqrt{3}C_h}{d_R}. \end{aligned} \quad (2-16-6)$$

Shotaro Maruyama (shotaro.maruyama@cmpt.phys.tohoku.ac.jp) (2/3/12)

Q:3-3 We consider $N - 1$ atoms attached between the two walls. When we consider x_0 and x_n as the coordinates of the two walls, show that all the equations of motion are expressed by the same formula. Then considering that the Bloch theorem applies, substitute $x_l = A \exp(iqla - i\omega t)$ into the equations of motion and obtain the dispersion of the phonon frequency $\omega(q)$. Plot dispersion of the phonon within the first Brillouin zone.

Answer: The equations of motion for the displacement of the l -th atom is given by

$$M_i \ddot{x}_l = -2K(x_l - x_{l-1} - x_{l+1}), \quad (3-3-1)$$

where M and K are, respectively, the mass and the force constant. Using x_l , the Eq. (3-3-1) can be written as

$$-M\omega^2 x_l = -2K(1 - \exp(-iqa) - \exp(iqa)) x_l, \quad (3-3-2)$$

where q and a are, respectively, the wave number and the lattice constant. For the boundary conditions that the end atoms are fixed, $\text{Re}(x_0)$ and $\text{Re}(x_N)$ are zero. When we consider $t = 0$, $\text{Re}(x_0) = 0$ is written as

$$\text{Re}(A) = 0. \quad (3-3-3)$$

From Eq. (3-3-3), A is purely imaginary number and satisfies Eq. (3-3-4);

$$A = iB, \quad (3-3-4)$$

where B is real number. Similarly, from $\text{Re}(x_N) = 0$, the $\text{Re}(x_N)$ is written as

$$\begin{aligned} \text{Re}(x_N) &= -iB \sin(qna) \\ &= 0 \end{aligned} \quad (3-3-5)$$

The wave number satisfy Eq. (3-3-6);

$$q = \frac{m\pi}{Na} \quad (m = 1, 2, \dots, N - 1). \quad (3-3-6)$$

The first Brillouin zone is given by

$$-\frac{\pi}{a} < q < \frac{\pi}{a}. \quad (3-3-7)$$

From Eq. (3-3-2), ω is obtained by

$$\omega = 2\sqrt{\frac{K}{M}} \left| \sin\left(\frac{qa}{2}\right) \right|. \quad (3-3-8)$$

In Fig. (3-3-1), the Eq. (3-3-8) is plotted within the first Brillouin zone, where ω_0 is defined by $2\sqrt{\frac{K}{M}}$.

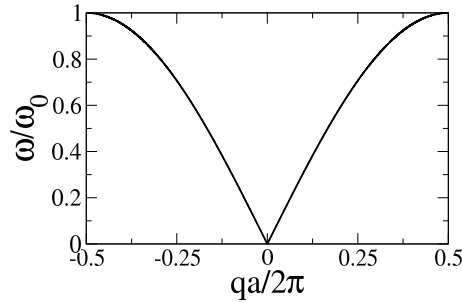


Figure 3-3-1: Dispersion of frequency

Kouki Yonaga (yona@cmpt.phys.tohoku.ac.jp) (12/7/11)

Q:3-8 In Figure 3.3, choose any unit cell vibrational mode and show that the motion of the atoms for $q = 0$ ($\lambda \rightarrow \infty$) and for $q = 2\pi/a$ ($\lambda = a$) is the same.

Answer: Let us consider 1D crystal system that has a $2N$ linear chain of atoms in which two different atoms A and B in the unit cell. If we use the Broch theorem, motions of two different atoms are in j -th unit cell written as

$$x_j^i(q) = A^i \exp(iqja), \quad (i = A, B, \text{ and } j = 1, 2, \dots, N), \quad (3-8-1)$$

where $x_j^i(q)$, a , q and A^i are, respectively, the displacement of A (B) atom, lattice constant, wave numbers and amplitude of A (B) atom. The first Brillouin zone is given by

$$-\frac{\pi}{a} < q < \frac{\pi}{a}, \quad (3-8-2)$$

which is defined by the smallest basic region in k -space. When we consider $q = 0$ and $q = 2\pi/a$, $x_j^i(q)$ is obtained by

$$\begin{aligned} x_j^i(0) &= A^i \exp(0) = A^i, \\ x_j^i(2\pi/a) &= A^i \exp(2\pi j) = A^i. \end{aligned} \quad (3-8-3)$$

Therefore, at $q = 0$ and $q = 2\pi/a$, the motion of atoms is the same (Fig.(3-8-1)).

Kouki Yonaga (yona@cmpt.phys.tohoku.ac.jp) (12/7/11)

Q:3-11 Consider a $2(N - 1)$ linear chain of atoms in which two different atoms A and B with masses M_A and M_B are connected along a chain (wall-A-B...-B-wall). Obtain and plot the phonon dispersion for this configuration.

Answer: The equations of motion for the displacement of the j -th atoms are given by

$$\begin{aligned} M_A \ddot{x}_j &= -K(x_j - y_{j-1}) - K(x_j - y_j) \\ M_B \ddot{y}_j &= -K(y_j - x_j) - K(y_j - x_{j+1}). \end{aligned} \quad (3-11-1)$$

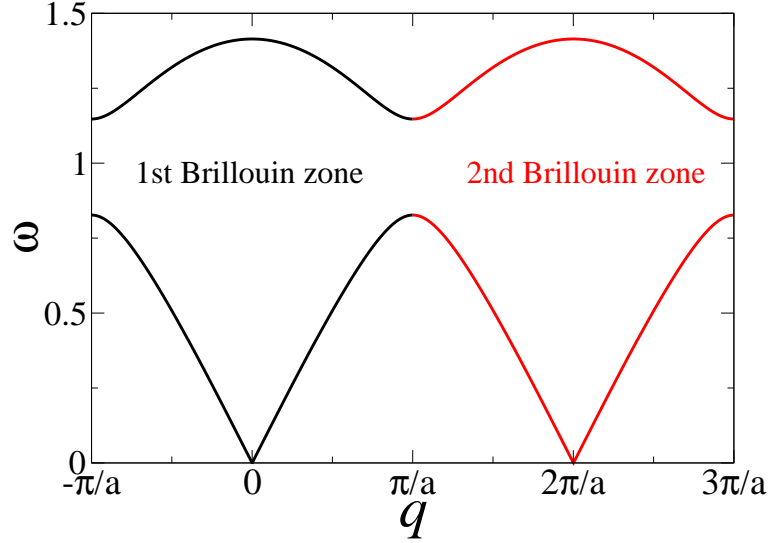


Figure 3-8-1: Schematic phonon dispersion relation of two atoms in the unit cell in the first Brillouin zone (black) and the second Brillouin zone (red).

where x_j , y_j and K are, respectively, the displacements of two different atoms in j -th unit cell and force constant. When we consider the Bloch theorem, the x_j , y_j are written as

$$\begin{aligned} x_j &= A \exp(i2kja - i\omega t) \\ y_j &= B \exp(i2kja - i\omega t). \end{aligned} \quad (3-11-2)$$

where A , B represent amplitude, and k and a are, respectively, the wave number and lattice constant. For the boundary conditions that the end atoms are fixed, $\text{Re}(x_N)$ and $\text{Re}(x_0)$ are zero. When we consider $t = 0$, $\text{Re}(x_0)$ is written as

$$\text{Re}(A) = 0. \quad (3-11-3)$$

From Eq. (3-11-3), A is a purely imaginary number and satisfies

$$A = iR, \quad (3-11-4)$$

where R is real number. From $\text{Re}(x_N) = 0$, the $\text{Re}(x_N)$ is written as

$$\text{Re}(x_N) = -iR \sin(kNa) = 0. \quad (3-11-5)$$

The wave numbers which satisfy Eq. (3-11-5) are given by

$$k = \frac{m\pi}{Na}, \quad (m = 1, 2, \dots, N-1). \quad (3-11-6)$$

Since length of the unit cell is $2a$, the first Brillouin zone is defined by a region in the k -space;

$$-\frac{\pi}{2a} < k < \frac{\pi}{2a}. \quad (3-11-7)$$

Using Eq. (3-11-1), Eq. (3-11-2) can be written as

$$\begin{aligned} -\omega^2 M_A A &= -2KA + K(1 + e^{-i2ka})B \\ -\omega^2 M_B B &= K(1 + e^{i2ka})A - 2KB. \end{aligned} \quad (3-11-8)$$

From Eq. (3-11-8), the simultaneous equations of motion can be expressed by

$$D(k)\mathbf{u} = 0, \quad (3-11-9)$$

where $D(k)$ and \mathbf{u} are defined, respectively, by

$$D(k) = \begin{bmatrix} -\frac{2K}{M_A} + \omega^2 & \frac{K}{M_B}(1 + e^{i2ka}) \\ \frac{K}{M_A}(1 + e^{-i2ka}) & -\frac{2K}{M_B} + \omega^2 \end{bmatrix}, \quad (3-11-10)$$

and

$$\mathbf{u} = \begin{bmatrix} A \\ B \end{bmatrix}. \quad (3-11-11)$$

To obtain the eigenvalues $\omega^2(k)$ for dynamical matrix with $\mathbf{u} \neq 0$, we solve a secular equation

$$\begin{vmatrix} -\frac{2K}{M_A} + \omega^2 & \frac{K}{M_B}(1 + e^{i2ka}) \\ \frac{K}{M_A}(1 + e^{-i2ka}) & -\frac{2K}{M_B} + \omega^2 \end{vmatrix} = 0. \quad (3-11-12)$$

From Eq. (3-11-12), we get ω_{\pm}^2 as follows;

$$\frac{\omega_{\pm}^2}{\omega_0^2} = 1 \pm \sqrt{1 - \frac{4M_A M_B \sin^2(ka)}{(M_A + M_B)^2}}, \quad (3-11-13)$$

where ω_0 is defined by $\omega_0 = \sqrt{K \left(\frac{1}{M_A} + \frac{1}{M_B} \right)}$. When we denote M_B with a positive number l

$$M_B = lM_A, \quad (3-11-14)$$

we get the ω_{\pm} ;

$$\begin{aligned} \frac{\omega_+}{\omega_0} &= \sqrt{1 + \sqrt{1 - \frac{4l \sin^2(ka)}{(1+l)^2}}} \\ \frac{\omega_-}{\omega_0} &= \sqrt{1 - \sqrt{1 - \frac{4l \sin^2(ka)}{(1+l)^2}}}. \end{aligned} \quad (3-11-15)$$

In Fig. (3-11-1), $\frac{\omega_+}{\omega_0}$ and $\frac{\omega_-}{\omega_0}$ are plotted within the first Brillouin zone. Here we consider the case that

$$\frac{4l}{(1+l)^2} = 0.9.$$

The ω_+ and ω_- are called, respectively, optical mode and acoustic mode. When we define an energy gap $\Delta\omega$ at $k = \pm\frac{\pi}{a}$, $\Delta\omega$ is expressed by

$$\begin{aligned} \Delta\omega &= \frac{\omega_+^2}{\omega_0^2} - \frac{\omega_-^2}{\omega_0^2}, \\ &= 2\sqrt{1 - \frac{4l \sin^2(ka)}{(1+l)^2}} \\ &= 2\frac{|1-l|}{(1+l)^2}. \end{aligned} \quad (3-11-16)$$

$\Delta\omega$ is plotted as a function of l for $l > 1$. Fig. (3-11-2), here we consider $\sin ka = 1$. Fig. (3-11-2) shows that, when the atoms in unit cell is equal ($l = 1$), the gap becomes zero. In the limit of $l = \infty$, ω_+ and ω_- goes, respectively, $2\omega_0$ and 0

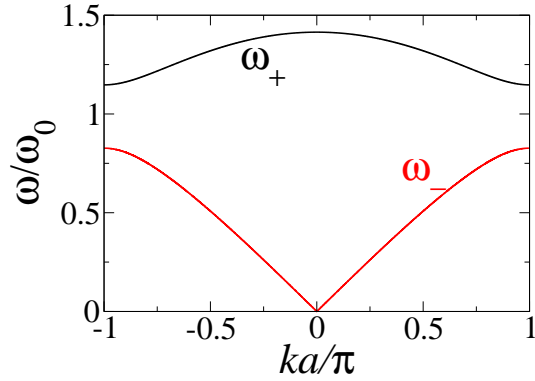
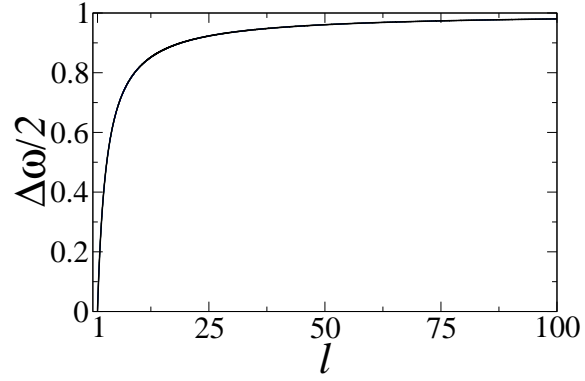


Figure 3-11-1: Energy Dispersion.

Figure 3-11-2: $\Delta\omega/2$ vs l .

Q:3-15 How many normal modes exist for the CH_4 , C_2H_2 and C_{60} molecules which, respectively, have the shapes of a regular tetrahedron, a linear chain, and a truncated icosahedron?

Answer: The molecular vibration M is defined by

$$M = 3N - d, \quad (3-15-1)$$

where N and d are, respectively, the number of atoms in the molecule and the degree of freedom that the molecule has. When we consider nonlinear molecules, M is written as

$$M = 3N - 6, \quad (3-15-2)$$

since nonlinear molecules have 3 translations and 3 rotations. When we consider linear molecules, M is written as

$$M = 3N - 5, \quad (3-15-3)$$

since linear molecules have 3 translations and only 2 rotations. Because, when we consider linear molecule along z axis, the rotation around the z axis does not exist. Since CH_4 is a nonlinear molecule, from Eq. (3-15-2), the number of the modes of CH_4 are given by

$$M = 3 \times 5 - 6 = 9. \quad (3-15-4)$$

Similarly, from Eq. (3-15-2), the modes of C_{60} are given by

$$M = 3 \times 60 - 6 = 174. \quad (3-15-5)$$

Since C_2H_2 is a linear molecule, from Eq. (3-15-3), the number of the modes of C_2H_2 are obtained by

$$M = 3 \times 4 - 5 = 7. \quad (3-15-6)$$

Kouki Yonaga (yona@cmpt.phys.tohoku.ac.jp) (12/7/11)

Q:4-2 Obtain Eq. (4.7) from Eq. (4.6).

Answer: Eq. (4.6) is given by

$$\chi \equiv \frac{P}{E} = \frac{\sum_j N_j \alpha_j}{1 - \frac{4\pi}{3} \sum_j N_j \alpha_j}, \quad (4-2-1)$$

where χ , P , E , N_j and α_j are the susceptibility, the polarization of crystal, the macroscopic electric field, the atomic concentration and the polarizability of each species, respectively. Using the relation of the dielectric constant and the susceptibility, $\varepsilon = 1 + 4\pi\chi$ (CGS), we calculate Eq. (4.6) as follows:

$$\begin{aligned}
\frac{\varepsilon - 1}{4\pi} &= \frac{\sum_j N_j \alpha_j}{1 - \frac{4\pi}{3} \sum_j N_j \alpha_j} \\
(\varepsilon - 1) \left(1 - \frac{4\pi}{3} \sum_j N_j \alpha_j \right) &= 4\pi \sum_j N_j \alpha_j \\
\varepsilon - 1 &= \left(\frac{4\pi}{3} \varepsilon - \frac{4\pi}{3} + 4\pi \right) \sum_j N_j \alpha_j \\
\varepsilon - 1 &= \frac{4\pi}{3} (\varepsilon + 2) \sum_j N_j \alpha_j \\
\frac{\varepsilon - 1}{\varepsilon + 2} &= \frac{4\pi}{3} \sum_j N_j \alpha_j. \tag{4-2-2}
\end{aligned}$$

Then we obtain “the Clausius-Mossotti relation” Eq. (4.7) which relates the dielectric constant and the electric polarizability, but only for crystal structures for which the Lorentz local field relation applies.

Yuki Tatsumi (tatsumi@flex.phys.tohoku.ac.jp) (01/16/12)

Q:4-4 Show that 1 eV corresponds to 8065 cm^{-1} . What is the energy in eV for the G-band Raman spectrum of graphite at 1580 cm^{-1} ?

Answer: The energy of a photon E is given by

$$E = h\omega = hck, \tag{4-4-1}$$

where h , ω , c , and k are Planck’s constant, the angular frequency of light, the velocity of light and the wave number of light ($k = 1/\lambda$ λ : wavelength of light), respectively. Planck’s constant and the velocity of light is given by

$$h = 6.6262 \times 10^{-34} \text{ J}\cdot\text{s}, \tag{4-4-2}$$

$$c = 2.9979 \times 10^8 \text{ m/s} = 2.9979 \times 10^{10} \text{ cm/s}. \tag{4-4-3}$$

Using $1 \text{ eV} = 1.602 \times 10^{-16} \text{ J}$, the wave number which corresponds to 1 eV is obtained from Eq. (4-4-1) as follows:

$$\begin{aligned}
E &= hck \\
1.602 \times 10^{-16} &= (6.6262 \times 10^{-34}) \times (2.9979 \times 10^{10}) \times k \\
k &= 8065 \text{ cm}^{-1}. \tag{4-4-4}
\end{aligned}$$

Then it is shown that 1 eV corresponds to 8065 cm^{-1} . What wavenumber the G-band Raman spectrum of graphite at 1580 cm^{-1} corresponds to is obtained as follows:

$$\begin{aligned} 1 : 8065 &= x : 1580 \\ x &= 0.196 \text{ eV}. \end{aligned} \quad (4-4-5)$$

Thus the G-band Raman spectrum of graphite at 1580 cm^{-1} corresponds to 0.196 eV .

Yuki Tatsumi (tatsumi@flex.phys.tohoku.ac.jp) (01/16/12)

Q:4-5 Obtain the energy in eV of a laser with a wavelength of 633 nm . What is the conversion formula from nm to eV and from eV to nm?

Answer: It is shown that 1 eV corresponds to 8065 cm^{-1} in Q4-4. Then the units of energy is converted from eV to nm^{-1} as follows:

$$1 \text{ eV} = 8065 \text{ cm}^{-1} = 8065 \times 10^{-7} \text{ nm}^{-1}. \quad (4-5-1)$$

The relation between the wavenumber and the wavelength is given by

$$k = \frac{1}{\lambda}, \quad (4-5-2)$$

where λ and k are the wavelength and the wavenumber, respectively. Using Eqs. (4-5-1) and (4-5-2), the energy in eV of a laser with a wavelength of 633 nm is written as follows:

$$E = \frac{1/633}{8065 \times 10^{-7}} = 1.96 \text{ eV}. \quad (4-5-3)$$

The conversion formula from $\lambda \text{ nm}$ to $E \text{ eV}$ and that from $E \text{ eV}$ to $\lambda \text{ nm}$ are written by

$$E = \frac{k}{8065 \times 10^{-7}} = \frac{10^7}{8065\lambda} = \frac{1239.9}{\lambda} \text{ eV}, \quad (4-5-4)$$

or

$$\lambda = \frac{10^7}{8065E} = \frac{1239.9}{E} \text{ nm}. \quad (4-5-5)$$

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Q:5-3 When we consider the Hamiltonian in the presence of a vector potential, expand the Hamiltonian and retain the linear term in \mathbf{A} . This corresponds to a perturbation Hamiltonian for the electron-photon coupling constant. Use the Coulomb gauge $\text{div} \mathbf{A} = 0$ when you obtain this result.

Answer: We consider an electron in the presence of a vector potential \mathbf{A} . Since the charge of an electron is $-e$, the form of the Hamiltonian for the electron is given by

$$\begin{aligned} H &= \frac{1}{2m} (\mathbf{p} + e\mathbf{A})^2 + V(\mathbf{r}) \\ &= \frac{1}{2m} (-i\hbar\nabla + e\mathbf{A})^2 + V(\mathbf{r}) \\ &= \frac{1}{2m} (-\hbar^2\Delta - ie\hbar\mathbf{A} \cdot \nabla - ie\hbar\nabla \cdot \mathbf{A} + e^2\mathbf{A}^2) + V(\mathbf{r}). \end{aligned} \quad (5-3-1)$$

Since ∇ in the third term in the third row of Eq. (5-3-1) operates not only \mathbf{A} but wavefunctions, we can obtain the following equation:

$$\nabla \cdot \mathbf{A} = \text{div} \mathbf{A} + \mathbf{A} \cdot \nabla = \mathbf{A} \cdot \nabla, \quad (5-3-2)$$

if we use the fact that \mathbf{A} satisfies the Coulomb gauge $\text{div} \mathbf{A} = 0$. Substituting Eq. (5-3-2) into Eq. (5-3-1), the form of the Hamiltonian can be written as:

$$H = H_0 - \frac{ie\hbar}{m} \mathbf{A} \cdot \nabla + \frac{e^2 \mathbf{A}^2}{2m}, \quad (5-3-3)$$

where H_0 is defined by

$$H_0 = -\frac{\hbar^2}{2m} \Delta + V(\mathbf{r}). \quad (5-3-4)$$

From Eq. (5-3-3), we can obtain the linear term in \mathbf{A} of the Hamiltonian H_{eR} as follows:

$$H_{eR} = -\frac{ie\hbar}{m} \mathbf{A} \cdot \nabla. \quad (5-3-5)$$

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Q:5-4 In the previous problem, we also have a term which is proportional to \mathbf{A}^2 . In order to neglect this term, this term should be at least 1/10 smaller than the linear \mathbf{A} term. What is the corresponding value of the electric field? If \mathbf{A} gives an electric field above this value, we should then consider the nonlinear \mathbf{A}^2 effect of light.

Answer: When monochromatic visible light (wavelength λ_{light} , angular frequency $\omega = 2\pi c/\lambda_{\text{light}}$) enters a graphene layer, a π electron which exists near the K or K' points in the two-dimensional Brillouin zone absorbs the light. The relation between a vector potential \mathbf{A} and an electric field \mathbf{E} of the light can be written as:

$$\mathbf{A} = -\frac{i}{\omega} \mathbf{E} = -\frac{i\lambda_{\text{light}}}{2\pi c} \mathbf{E}, \quad (5-4-1)$$

by considering the Maxwell equation $\mathbf{E} = -\partial \mathbf{A} / \partial t$ and $\mathbf{A} \propto \exp(-i\omega t)$. From the Eq. (5-4-1), we get

$$\mathbf{A}^2 = -\left(\frac{\lambda_{\text{light}}}{2\pi c}\right)^2 \mathbf{E}^2. \quad (5-4-2)$$

From the Eq. (5.27) in the book, the perturbation Hamiltonian H_{eR} for an electron in the presence of the vector potential is given by

$$\begin{aligned} H_{eR} &= \frac{e}{m} \mathbf{A} \cdot \mathbf{p} + \frac{e^2}{2m} \mathbf{A}^2 \\ &= -\frac{ie\hbar}{m} \mathbf{A} \cdot \nabla + \frac{e^2}{2m} \mathbf{A}^2 \\ &= \frac{e\hbar}{m} \mathbf{A} \cdot \mathbf{k}_e + \frac{e^2}{2m} \mathbf{A}^2, \end{aligned} \quad (5-4-3)$$

where $\mathbf{p} = -i\hbar \nabla = \hbar \mathbf{k}_e$ is a momentum operator of an electron in vacuum. From the Eqs. (5-4-1) and (5-4-2), we can obtain the ratio R of the absolute value of the term in \mathbf{A}^2 of the Eq. (5-4-3) to the one of \mathbf{A} as follows:

$$R = \frac{\left| \frac{e^2}{2m} \mathbf{A}^2 \right|}{\left| \frac{e\hbar}{m} \mathbf{A} \cdot \langle \mathbf{k}_e \rangle \right|} = \frac{\frac{e^2}{2m} \left(\frac{\lambda_{\text{light}}}{2\pi c} \right)^2}{\frac{e\hbar}{m} \frac{\lambda_{\text{light}}}{2\pi c}} \frac{|\mathbf{E}^2|}{|\mathbf{E} \cdot \langle \mathbf{k}_e \rangle|} = \frac{e\lambda_{\text{light}}}{2\pi\hbar c} \frac{|\mathbf{E}^2|}{|\mathbf{E} \cdot \langle \mathbf{k}_e \rangle|} \simeq \frac{e\lambda_{\text{light}}}{2\pi\hbar c} \frac{|\mathbf{E}|}{|\langle \mathbf{k}_e \rangle|}, \quad (5-4-4)$$

where $\langle \mathbf{k}_e \rangle$ is the average of \mathbf{k}_e . Using Eq.(5-4-4) the corresponding thresfold value of the electric field $|\mathbf{E}_{\text{th}}|$ for $R = 1/10$ can be written as:

$$|\mathbf{E}_{\text{th}}| = \frac{\pi\hbar c}{5e\lambda_{\text{light}}} |\langle \mathbf{k}_e \rangle|. \quad (5-4-5)$$

The wavenumber of the electron around the K and K' points in the graphene layer $|\langle \mathbf{k}_e \rangle|$ can be approximated as follows:

$$|\langle \mathbf{k}_e \rangle| \simeq |\mathbf{k}_F| = \frac{m}{\hbar} v_F, \quad (5-4-6)$$

where \mathbf{k}_F is the Fermi wave vector and v_F is the Fermi velocity of the π electron in the graphene layer. From Eq.(2.34) in the book, v_F is given by

$$v_F = \frac{3\gamma_0 a_{c-c}}{2\hbar}, \quad (5-4-7)$$

where $a_{c-c} = 0.142 \text{ nm}$ is the nearest neighbor carbon-carbon distance and $t = -\gamma_0 = -3.033 \text{ eV}$ is the nearest neighbor transfer integral. Using the Eqs. (5-4-5), (5-4-6) and (5-4-7), we can obtain the thresfold value of the electric field of the monochromatic visible light ($3.8 \leq \lambda_{\text{light}} \leq 7.5$ in the units of 10^{-7} m) in the units of $\text{V} \cdot \text{m}^{-1}$ as follows:

$$|\mathbf{E}_{\text{th}}| = \frac{3\pi m c \gamma_0 a_{c-c}}{10e\hbar\lambda_{\text{light}}}, \quad (5-4-8)$$

above which we should consider the nonlinear effect of light. In the case of $\lambda_{\text{light}} = 750 \text{ nm}$, $|\mathbf{E}_{\text{th}}| = 2.4 \times 10^9 \text{ V} \cdot \text{m}^{-1}$.

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Q:5-5 The Poynting vector, $\vec{S} = \vec{E} \times \vec{H}$ is the power density per unit area of the electromagnetic field. In a typical micro-Raman measurement system, the diameter of the light beam is about $1 \mu\text{m}$ and the laser power is 1 mW . Estimate the power density of this micro-Raman setup and calculate \vec{E} . Show that the electric field thus obtain is not strong enough to be in the non-linear regime.

Answer: Using $|\vec{B}| = |\vec{E}|/c$, we get a formula for $|\vec{S}|$.

$$\begin{aligned} |\vec{S}| &= |\vec{E}||\vec{H}| \sin \frac{\pi}{2} \\ &= \frac{1}{\mu_0} |\vec{E}||\vec{B}| \\ &= \frac{1}{\mu_0 c} |\vec{E}|^2, \end{aligned} \quad (5-5-1)$$

where μ_0 is absolute permeability of vacuum. We also get the following equation from the numerical value given by Q5-5 as follows:

$$|\vec{S}| = \frac{10^{-3}}{\pi(0.5 \times 10^{-6})^2} \text{Wm}^{-2}. \quad (5-5-2)$$

Using Eqs. (5-5-1) and (5-5-2), we obtain the magnitude of \vec{E} as follows:

$$\begin{aligned}
 |\vec{E}|^2 &= \mu_0 c \times \frac{10^{-3}}{\pi(0.5 \times 10^{-6})^2} \\
 &= (4\pi \times 10^{-7}) \times c \times \frac{10^{-3}}{\pi(0.5 \times 10^{-6})^2} \\
 &= 4.78 \times 10^{11} \text{ V}^2\text{m}^{-2}.
 \end{aligned} \tag{5-5-3}$$

Using Eq. (5-5-3), we get

$$|\vec{E}| = 6.9 \times 10^5 \text{ Vm}^{-1}, \tag{5-5-4}$$

where $\mu_0 = 4\pi \times 10^{-7} \text{ N/A}^2$, $c = 2.99 \text{ m/s}$. In the previous problem Q5-4, we show the numerical value where we can neglect the non-linear term of \vec{E} . According to the result, the electric field is not strong enough to be in the non-linear term when the magnitude of \vec{E} is smaller than 10^9 Vm^{-1} . The numerical value in Eq. (5-5-3) satisfies the condition and we can neglect the higher term of $|\vec{E}|$.

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