Solutions for Assignment #1

Note Title

1. (C+L 2.1)

Use $S(q) = \frac{1}{N}\left\langle \sum_{ij} e^{-iq(x_i - x_j)} \right\rangle$

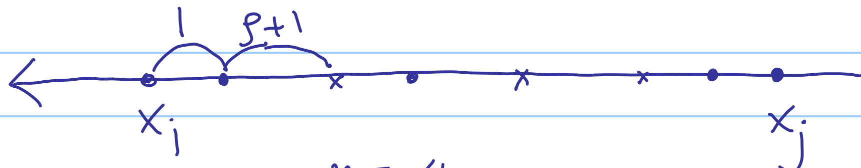
Consider $i<j$:

m : mass points separation between x_i and x_j

For each m separation $\Rightarrow$ # of ρ : n

of $\rho+1$: $m-n$

Example: when $m=7$



$n=4$

$m-n=3$

Then the exponent becomes

$+iq\left[n + (m-n)(\rho+1)\right]$ for $i<j$

$-iq\left[n + (m-n)(\rho+1)\right]$ for $i>j$

For completely random distribution, the probability is $\frac{m!}{n!(m-n)!} p^n (1-p)^{m-n}$

$$S(q) = \left\langle \sum_{ij} e^{-iq(x_i - x_j)} \right\rangle$$

$$= \sum_{m=0}^{\infty} \sum_{n=0}^{m} \frac{m!\, p^n (1-p)^{m-n}}{n!(m-n)!} e^{iq[n+(m-n)(\rho+1)]}$$

$$+\sum_{m=1}^{\infty}\sum_{n=0}^{m}\frac{m!\,p^{n}(1-p)^{m-n}}{n!\,(m-n)!}\,e^{-iq[n+(m-n)(\rho+1)]}$$

$$=\sum_{m=0}^{\infty}\left(pe^{iq}+(1-p)e^{iq(\rho+1)}\right)^{m}+\sum_{m=1}^{\infty}\left(pe^{-iq}+(1-p)e^{-iq(\rho+1)}\right)^{m}$$

(geometric series)

$$=\frac{1}{1-pe^{iq}-(1-p)e^{iq(\rho+1)}}+\frac{pe^{-iq}+(1-p)e^{-iq(\rho+1)}}{1-pe^{-iq}-(1-p)e^{-iq(\rho+1)}}$$

$$=\frac{A}{B}$$

$$A = 1\cancel{-pe^{-iq}}\cancel{-(1-p)e^{-iq(\rho+1)}}\cancel{+pe^{-iq}}-p^{2}-p(1-p)e^{iq\rho}\cancel{+(1-p)e^{-iq(\rho+1)}}$$
$$-p(1-p)e^{-iq\rho}-(1-p)^{2}$$

$$=\cancel{1}-p^{2}-(\cancel{1}-2p+p^{2})-p(1-p)\left(e^{iq\rho}+e^{-iq\rho}\right)$$

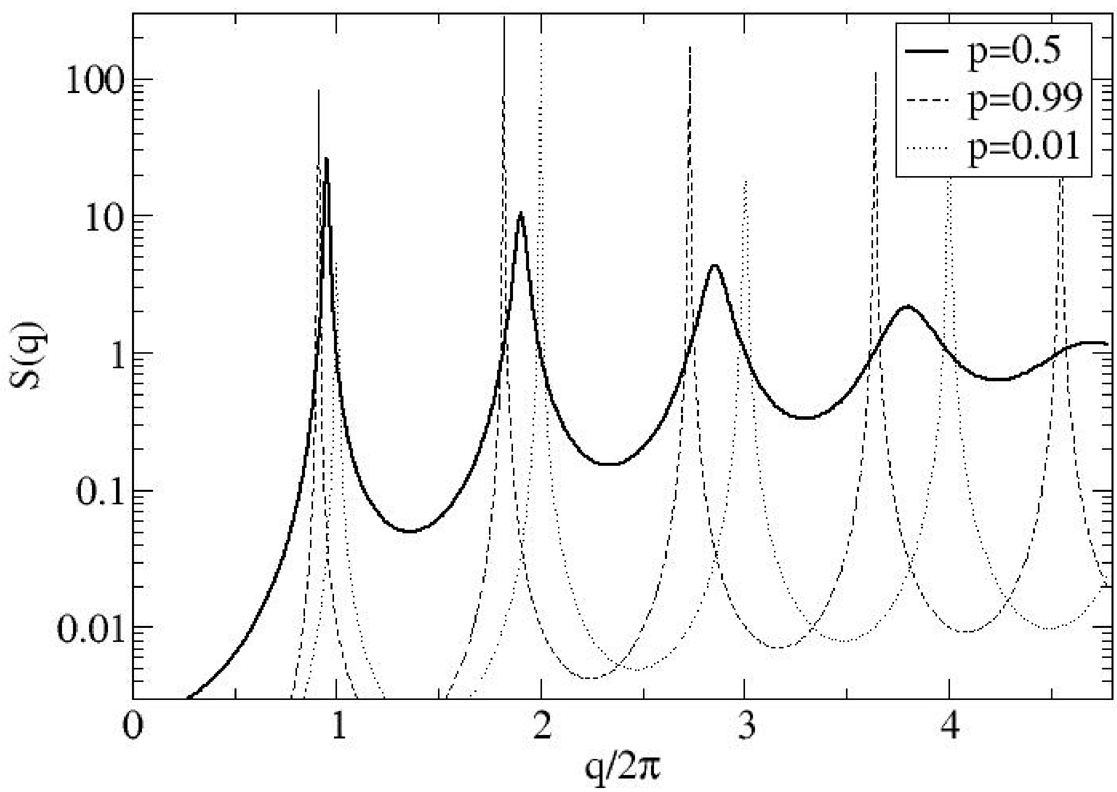
$$=2p(1-p)-2p(1-p)\cos\rho q=2p(1-p)(1-\cos\rho q)$$

$$B=1+p^{2}+(1-p)^{2}-p\left(e^{iq}+e^{-iq}\right)-(1-p)\left(e^{iq(\rho+1)}+e^{-iq(\rho+1)}\right)$$
$$+p(1-p)\left(e^{iq\rho}+e^{-iq\rho}\right)$$

$$=2(1-p+p^{2})-2p\cos q-2(1-p)\cos\left(q(\rho+1)\right)+2p(1-p)\cos\rho q$$

$$\therefore S(q)=\frac{p(1-p)(1-\cos\rho q)}{1-p(1-p)-p\cos q-(1-p)\cos\left(q(\rho+1)\right)+p(1-p)\cos\rho q}$$

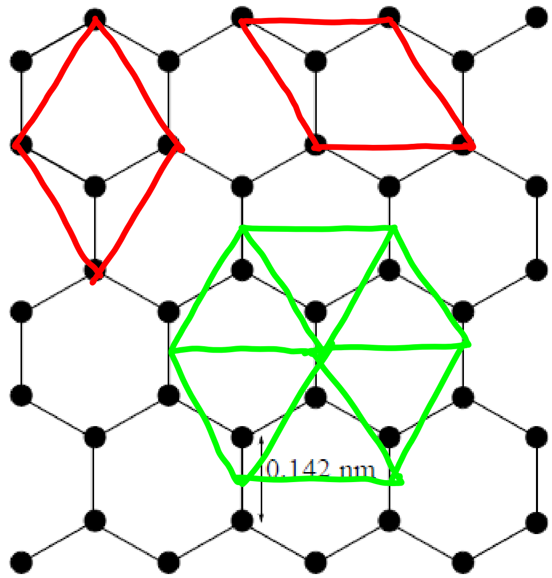
This Hendrix–Teller model for random alloy is used often to describe random mixture of two structures. Example of the structure factor are shown here.



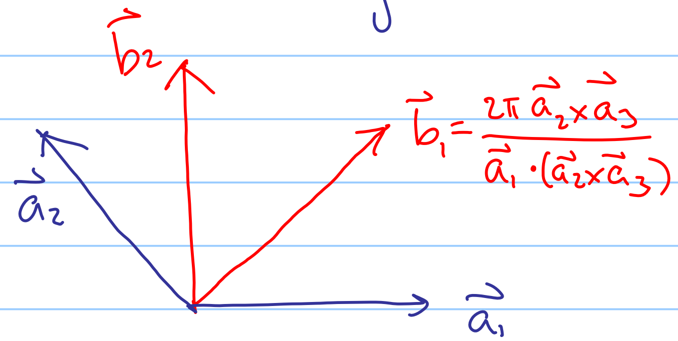
The dashed lines are 99% and 1% plot (two extreme ends) Equal mixture of these two structures end up giving broad peaks centered at the intermediate positions.

2. (graphene)

(a) There is no single answer to this question. As long as you have two atoms in a cell that can be tiled together to form the lattice will do.



Unit cell (red lines) forms a hexagonal lattice as shown in green.



($\because$ $\vec{a}_3 \perp$ to the plane)

Note that $\vec{b}_1$, and $\vec{b}_2$ forms 60° instead of 120°.

It is very confusing to work on hexagonal lattice using $\vec{a}_i$ and $\vec{b}_i$. Expressing these in Cartesian coordinates will make things much easier.

Then,

$$\vec{a}_1 = a\,\hat{x}$$

$$\vec{a}_2 = a\left(-\frac{1}{2}\hat{x} + \frac{\sqrt{3}}{2}\hat{y}\right)$$

$a = 1.42 \cdot \sqrt{3} = \underline{\underline{2.46\,\mathring{A}}}$

$$\vec{a}_3 = c\,\hat{z}$$

(c is not important here, just the direction)

$$\vec{a}_2 \times \vec{a}_3 = ac\left(\frac{1}{2}\hat{y} + \frac{\sqrt{3}}{2}\hat{x}\right)$$

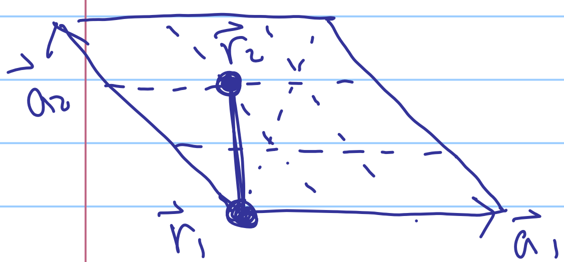
$$\vec{a}\cdot(\vec{a}_2 \times \vec{a}_3) = a^2 c\,\frac{\sqrt{3}}{2} = \text{volume of unit cell}$$

$$\vec{b}_1 = \frac{2\pi\, \vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} = \frac{2\pi\, \cancel{a c}\left(\frac{\sqrt{3}}{2}\hat{x} + \frac{1}{2}\hat{y}\right)}{a^2 \cancel{c}\left(\sqrt{3}/2\right)} = \frac{4\pi}{\sqrt{3}}\left(\frac{\sqrt{3}}{2}\hat{x} + \frac{1}{2}\hat{y}\right)$$

$$\vec{b}_2 = \frac{4\pi}{\sqrt{3}}\hat{y}$$

(b) In one unit cell there are two carbon atoms:

$$\vec{r}_1 = 0, \quad \vec{r}_2 = \frac{1}{3}\vec{a}_1 + \frac{2}{3}\vec{a}_2$$



$$= \cancel{\frac{1}{3}a\hat{x}} - \cancel{\frac{2}{3}\frac{a}{2}\hat{x}} + \frac{a}{\sqrt{3}}\hat{y}$$

Note the $\frac{\pi}{3}$ rotational symmetry in the reciprocal space.

The bond direction is then $\pm\vec{b}_1, \pm\vec{b}_2, \vec{b}_1 - \vec{b}_2$, or $-\vec{b}_1 + \vec{b}_2$.

The diretion $\perp$ to the bond is then $\vec{b}_1 + \vec{b}_2$, $-\vec{b}_1 - \vec{b}_2$ ....etc.

Let's choose $\hat{y}$ direction (bond dir.)

$\hat{x}$ - direc ($\perp$ to bond)

$$\vec{q} = q_x\hat{x} \text{ or } q_y\hat{y}$$

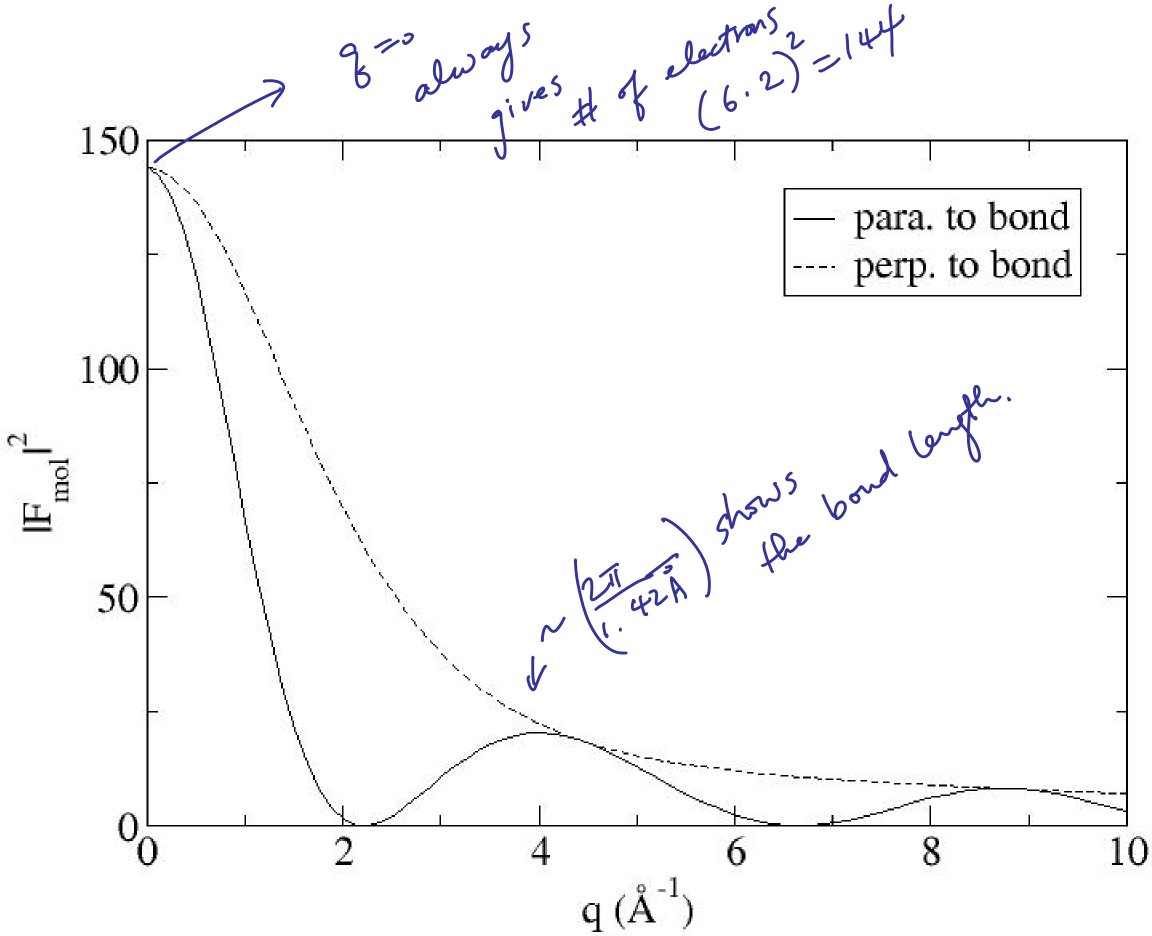
$$\vec{q}\cdot\vec{r}_1 = 0 \qquad \vec{q}\cdot\vec{r}_2 = \begin{cases} 0 \\ \dfrac{q_y a}{\sqrt{3}} \end{cases}$$

$$\therefore F^{mol}(q) = \sum_{r_j} f_j(q)\, e^{i\vec{q}\cdot\vec{r}_j}$$

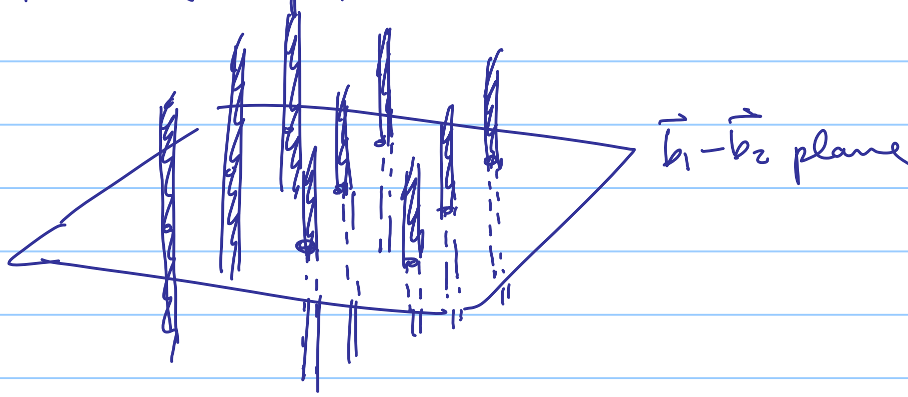
$$= \begin{cases} f_c(q_x)\cdot 2 \\ f_c(q_y)\left(1 + e^{i\frac{q_y a}{\sqrt{3}}}\right) \end{cases}$$

$$|F|^2 = \begin{cases} 4 f_c^2 \\ f_c^2 \left(2 + 2\cos \frac{q_y a}{\sqrt{3}}\right) = 4 f_c^2 \cos^2\left(\frac{q_y a}{2\sqrt{3}}\right) \end{cases}$$

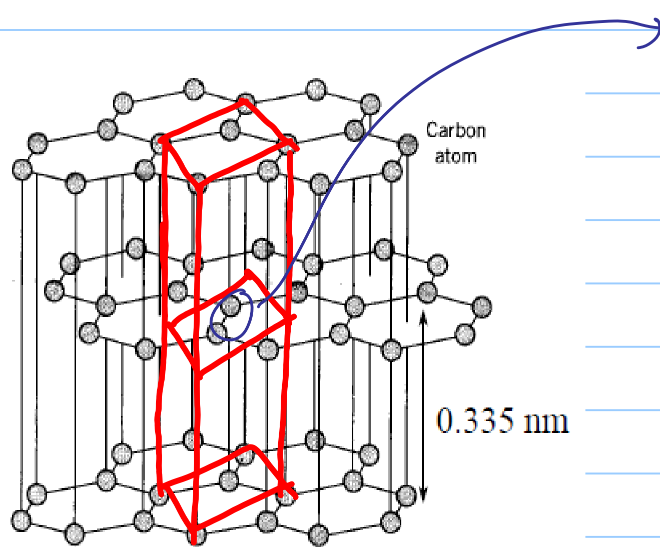
Atomic form factors can be found in International Tables of Crystallography Vol C. Chap 6.1 pp. 554–595



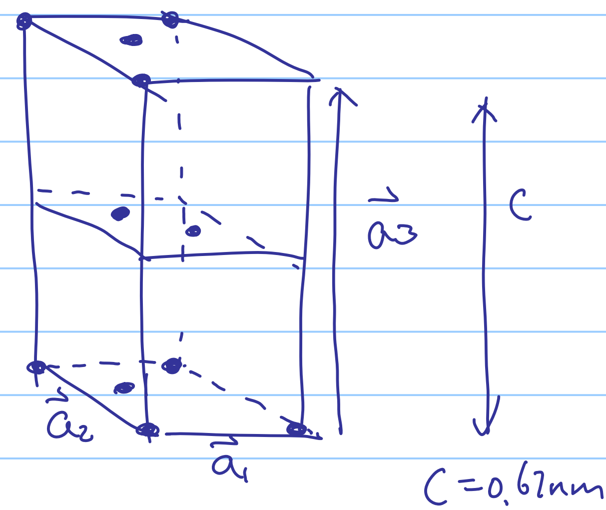
(c) The Bragg peak in the c-direction will be elogated to form a rod of scattering intensity rather than a spot.



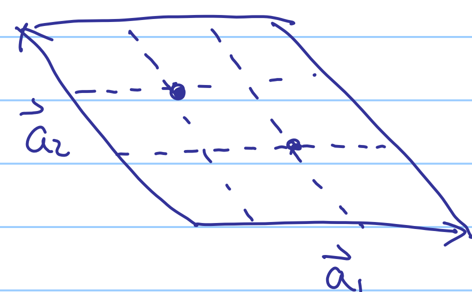
(d)



Two additional atoms are in 3D unit cell.



For $c/2$ plane



and now $\vec{r}_3 = \frac{1}{3}\vec{a}_1 + \frac{2}{3}\vec{a}_2 + \frac{1}{2}\vec{a}_3$ $\quad \vec{r}_4 = \frac{2}{3}\vec{a}_1 + \frac{1}{3}\vec{a}_1 + \frac{1}{2}\vec{a}_3$

($\vec{r}_1$ and $\vec{r}_2$ remain the same)

$\vec{a}_3 = c\,\hat{z}\,, \quad \vec{b}_3 = \frac{2\pi}{c}\,\hat{z}$

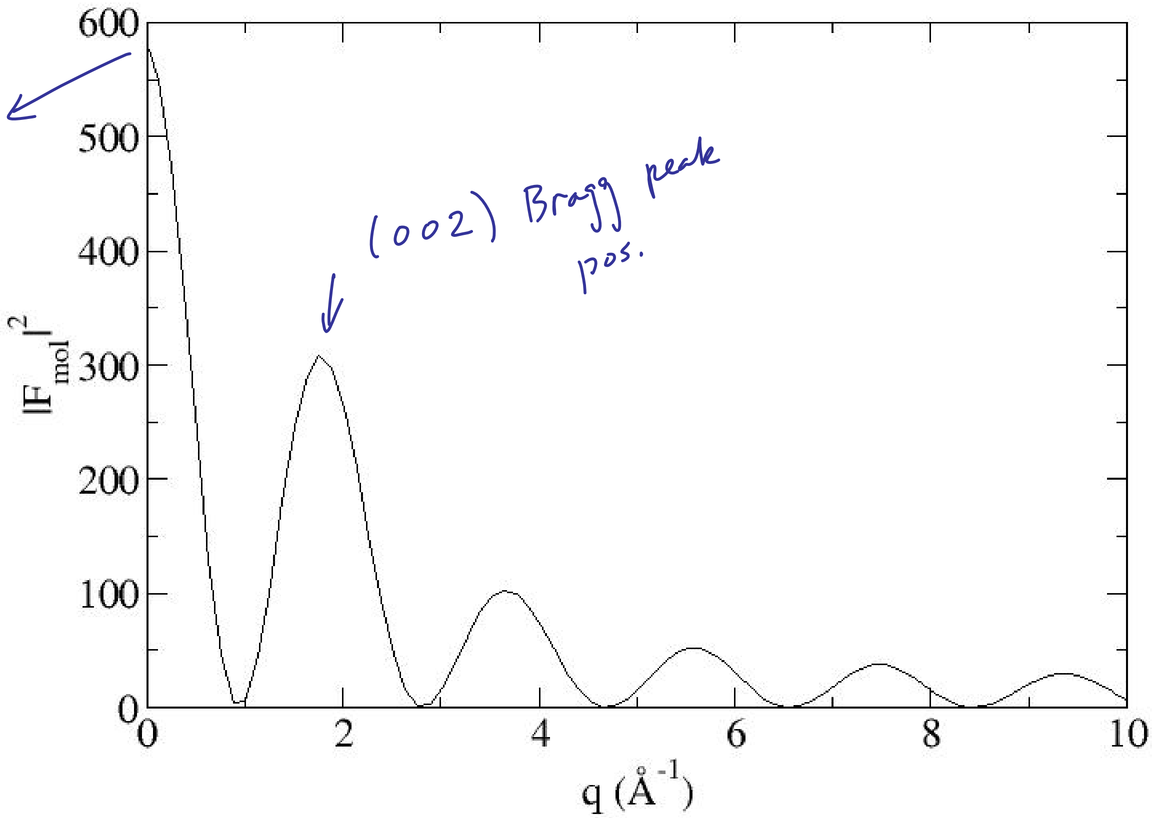
$\vec{q} = q\,\hat{z}\,,$ so $\vec{q}\cdot\vec{r}_j = \frac{qc}{2}$ for $\vec{r}_3$ and $\vec{r}_4$,

zero for $\vec{r}_1$ and $\vec{r}_2$

$$\therefore\ F^{mol}(q) = 2f_c(q)\cdot\left(1 + e^{iqc/2}\right)$$

$$|F^{mol}|^2 = 4f_c^2\left(2 + 2\cos\frac{qc}{2}\right) = 16 f_c^2 \cos^2\left(\frac{qc}{4}\right)$$

$(6\cdot 4)^2 = 576$



3. (a) Let's first consider the potential energy due to the point charge located at $(0,0,a)$:

$$V_z^+(x,y,z) = \frac{eQ}{\sqrt{x^2+y^2+(z-a)^2}}. \tag{1}$$

Since $x^2+y^2+(z-a)^2 = a^2[1-2\frac{z}{a}+(\frac{r}{a})^2]$, we can use the generating function of Legendre polynomials, with $t = r/a$ and $u = z/r$. Then,

$$\begin{aligned}
\frac{1}{\sqrt{x^2+y^2+(z-a)^2}} &= \frac{1}{a}\sum_{n=0}^{\infty}\left(\frac{r}{a}\right)^n P_n\left(\frac{z}{r}\right) \\
&= \frac{1}{a}\left[1+\frac{r}{a}\frac{z}{r}+\left(\frac{r}{a}\right)^2\frac{1}{2}\left(3\frac{z^2}{r^2}-1\right)+\left(\frac{r}{a}\right)^3\frac{1}{2}\left(5\frac{z^3}{r^3}-3\frac{z}{r}\right)\right. \\
&+ \left.\left(\frac{r}{a}\right)^4\frac{1}{8}\left(35\frac{z^4}{r^4}-30\frac{z^2}{r^2}+3\right)+...\right]
\end{aligned}$$

Therefore,

$$V_z^+(x,y,z) = \frac{Qe}{a}\left[1+\frac{z}{a}+\frac{1}{2a^2}\left(3z^2-r^2\right)+\frac{1}{2a^3}\left(5z^3-3zr^2\right)+\frac{1}{8a^4}\left(35z^4-30z^2r^2+3r^4\right)+...\right] \tag{2}$$

Now, if we add the contribution from the charge at $(0,0,-a)$, the terms in odd power of a vanish by symmetry. That is,

$$V_z = V_z^+ + V_z^- = \frac{2Qe}{a}\left[1+\frac{1}{2a^2}\left(3z^2-r^2\right)+\frac{1}{8a^4}\left(35z^4-30z^2r^2+3r^4\right)+...\right]. \tag{3}$$

If we add up all the contributions from the point charges, we obtain

$$\begin{aligned}
V_x+V_y+V_z &= \frac{2Qe}{a}\left[3+\frac{1}{2a^2}\left(3(x^2+y^2+z^2)-3r^2\right)\right. \\
&+ \left.\frac{1}{8a^4}\left(35(x^4+y^4+z^4)-30(x^2+y^2+z^2)r^2+9r^4\right)+...\right] \\
&= \frac{Qe}{a}\left[6+\frac{35}{4a^4}\left(x^4+y^4+z^4-\frac{3}{5}r^4\right)+O(r^6)\right],
\end{aligned} \tag{4}$$

using $r^2 = x^2+y^2+z^2$.

(b) In spherical coordinates, the second term in Eq. (7) can be converted to

$$V = \frac{35Qe}{4a^5}r^4\left[\sin^4\theta\frac{3+\cos 4\phi}{4}+\cos^4\theta-\frac{3}{5}\right]. \tag{5}$$

Using the wavefunctions given in the problem, the matrix elements can be calculated as follows.

$$\begin{aligned}
V_{22} &= \langle 2|V|2\rangle \\
&= \frac{35Qe}{4a^5}\int\int\int r^2\sin\theta drd\theta d\phi R(r)^2\sin^4\theta r^4\left[\sin^4\theta\frac{3+\cos 4\phi}{4}+\cos^4\theta-\frac{3}{5}\right] \\
&= \frac{35Qe}{4a^5}\int r^6R(r)^2dr\int_0^2\pi d\phi\int_0^{\pi}d\theta\sin^5\theta\left[\frac{3}{4}\sin^4\theta+\cos^4\theta-\frac{3}{5}\right].
\end{aligned}$$

Note that the $\cos 4\phi$ term vanishes under ϕ integration. Using $x \equiv \cos\theta$, we obtain for the θ integral

$$\int_{-1}^{1} dx(1-x^2)^2 \left[\frac{3}{4}(1-x^2)^2 + x^4 - \frac{3}{5}\right] = \frac{32}{1575}. \tag{6}$$

Then, for the matrix element,

$$V_{22} = \frac{35Qe}{4a^5} 2\pi \frac{32}{1575} \int r^6 R(r)^2 dr = Dq, \tag{7}$$

where $D \equiv 35eQ/4a^5$ and $q \equiv (64\pi/1575) \int r^6 R(r)^2 dr$. We can similarly work out the other matrix elements.

(c) The secular equation for the matrix V is obtained by setting the determinant of the matrix $(V - \lambda I)$ equals to zero:

$$(Dq-\lambda)^2(-4Dq-\lambda)^2(6Dq-\lambda) + 5Dq(-4Dq-\lambda)^2(6Dq-\lambda)(-5Dq) = 0. \tag{8}$$

This is simplified to

$$(4Dq+\lambda)^3(6Dq-\lambda)^2 = 0, \tag{9}$$

and we obtain doubly degenerate eigenvalue $6Dq$ and triply degenerate $-4Dq$.
By looking at the matrix, we can immediately recognize that $|0\rangle$ and $|\pm 1\rangle$ are eigenvectors with eigenvalues $6Dq$ and $-4Dq$, respectively. By plugging in the eigenvalues back to $(V - \lambda I)$, we obtain $a_2 = a_{-2}$ for $\lambda = 6Dq$. Therefore, the normalized eigenvector is $\frac{|2\rangle + |-2\rangle}{\sqrt{2}}$. Similarly, for $\lambda = -4Dq$, we obtain $a_2 = a_{-2}$, and the eigenvector becomes $\frac{|2\rangle - |-2\rangle}{\sqrt{2}}$.

4. High momentum resolution is required.
Synchrotron beam is highly collimating to begin with
→ good resolution with added benefit of intensity.