Section 4. Approximate methods for stationary states

i.e. V is not time dependent

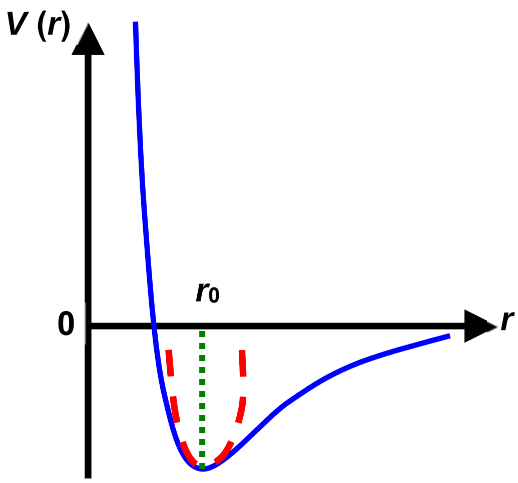
In this course and the year 2 course we have looked at examples where the TISE in 1D or 3D has exact solutions (infinite square well, finite square well, harmonic oscillator, H atom, etc).

- Introduce methods for cases where exact solutions cannot be found, in particular where the system is "close to" an exactly solvable case

- Non-degenerate perturbation theory

- Degenerate perturbation theory

Example Harmonic oscillator



Particle of mass m at the minimum of an interatomic potential $V(r)$

Use Taylor's theorem for small displacements $r - r_0$

$$V(r) = V(r_0) + (r - r_0)\cancelto{0}{\left.\frac{dV}{dr}\right|_{r_0}} + \frac{(r - r_0)^2}{2}\left.\frac{d^2V}{dr^2}\right|_{r_0}$$

$$\underbrace{+O\left[(r - r_0)^3\right]}_{\boxed{\text{anharmonic terms}}}$$

In the harmonic approximation, the force is given by

$$F(r) = -\frac{dV}{dr} = -(r - r_0)\left.\frac{d^2V}{dr^2}\right|_{r_0} \equiv -\underbrace{C}_{\text{spring constant}}(r - r_0)$$

which is the equation for a simple harmonic oscillator

If higher order terms describing anharmonic motion are small, we can treat them as a perturbation of the potential energy $V(r)$ for a simple harmonic oscillator

4.1 Non-degenerate perturbation theory

• Consider the case where the total energy (Hamiltonian) operator can be written as

$$\hat{H} = \hat{H}_0 + \hat{H}'$$

• $\hat{H}_0$ is the Hamiltonian of the "unperturbed" system, and we assume that we know its eigenvalues and eigenfunctions, i.e. solutions of

$$\hat{H}_0 \left| \phi_{0n} \right\rangle = E_{0n} \left| \phi_{0n} \right\rangle \qquad (1) \qquad \boxed{\text{TISE}}$$

• $\hat{H}'$ represents an additional energy term that acts as a "perturbation" on the system described by $\hat{H}_0$. We assume that it is small in comparison to $\hat{H}_0$.

Example: $\hat{H}_0$ could be the Hamiltonian for the H atom, and $\hat{H}'$ could be the effect of a weak electric field

• What is the effect of $\hat{H}'$ on the eigenvalues and eigenfunctions of $\hat{H}_0$ (i.e on E_{0n} and $|\phi_{0n}\rangle$)?

unperturbed

In this sub-section, we assume that $|\phi_{0n}\rangle$ is not degenerate, so E_{0n} is unique

We build up the solution in powers of $\hat{H}'$. To do this, it's helpful to write

$$\hat{H} = \hat{H}_0 + \lambda \hat{H}' \qquad (2)$$

constant that we will eventually set to 1

We look for solutions of

$$\hat{H}|\phi_n\rangle = E_n|\phi_n\rangle \qquad (3)$$

perturbed system

in the form

$$E_n = E_{0n} + \lambda E_{1n} + \lambda^2 E_{2n} + \cdots \qquad (4)$$

$$|\phi_n\rangle = |\phi_{0n}\rangle + \lambda|\phi_{1n}\rangle + \lambda^2|\phi_{2n}\rangle + \cdots \qquad (5)$$

first order corrections

second order corrections

• Substitute (4) and (5) into (3) and equate the terms with different powers of λ

$\boxed{\lambda^0 \text{ terms}}$

$$\hat{H}_0 |\phi_{0n}\rangle = E_{0n} |\phi_{0n}\rangle \qquad (6) \qquad \boxed{\text{as expected!}}$$

$$\hat{H}' |\phi_{0n}\rangle + \hat{H}_0 |\phi_{1n}\rangle = E_{0n} |\phi_{1n}\rangle + E_{1n} |\phi_{0n}\rangle \qquad (7)$$

$\boxed{\lambda^1 \text{ terms}}$

$$\hat{H}' |\phi_{1n}\rangle + \hat{H}_0 |\phi_{2n}\rangle = E_{0n} |\phi_{2n}\rangle + E_{1n} |\phi_{1n}\rangle + E_{2n} |\phi_{0n}\rangle$$

$\boxed{\lambda^2 \text{ terms}}$ (8)

Write the first order correction $|\phi_{1n}\rangle$ as

$$|\phi_{1n}\rangle = \sum_k a_{nk} |\phi_{0k}\rangle \qquad (9)$$

[This is an eigenfunction expansion, as in section 1.5. The coefficient a_{nk} gives the "amount" of $|\phi_{0k}\rangle$ in $|\phi_{1n}\rangle$.]

• Substitute (9) into (7) and use (6) to get

$$\left(\hat{H}' - E_{1n}\right)\left|\phi_{0n}\right\rangle = \sum_k a_{nk}\left(E_{0n} - E_{0k}\right)\left|\phi_{0k}\right\rangle$$

used $\hat{H}_0\left|\phi_{1n}\right\rangle = \sum_k a_{nk} E_{0k}\left|\phi_{0k}\right\rangle$

• "Close" both sides with $\left\langle\phi_{0n}\right|$. Because of orthogonality, $\left\langle\phi_{0n}\middle|\phi_{0k}\right\rangle = \delta_{nk}$, and the r.h.s. is zero. The l.h.s. gives

If $n = k$, $E_{0n} - E_{0k} = 0$

If $n \neq k$, $\left\langle\phi_{0n}\middle|\phi_{0k}\right\rangle = 0$

$$\boxed{E_{1n} = \left\langle\phi_{0n}\middle|\hat{H}'\middle|\phi_{0n}\right\rangle} \qquad (10)$$

In 1D this becomes

$$E_{1n} = \int \phi_{0n}^*(x)\,\hat{H}'(x)\,\phi_{0n}(x)\,dx$$

In 3D this becomes

$$E_{1n} = \iiint \phi_{0n}^*(\underline{r})\,\hat{H}'(\underline{r})\,\phi_{0n}(\underline{r})\,d^3r$$

This process can be continued. We eventually find

first order

$$E_n = E_{0n} + \langle \phi_{0n} | \hat{H}' | \phi_{0n} \rangle$$

$$+ \sum_{k \neq n} \frac{\langle \phi_{0n} | \hat{H}' | \phi_{0k} \rangle \langle \phi_{0k} | \hat{H}' | \phi_{0n} \rangle}{E_{0n} - E_{0k}} + \cdots \quad (11)$$

second order

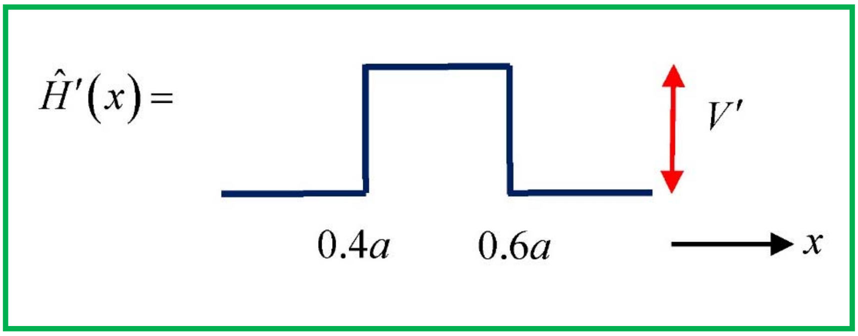
$$|\phi_n\rangle = |\phi_{0n}\rangle + \sum_{k \neq n} \frac{\langle \phi_{0k} | \hat{H}' | \phi_{0n} \rangle}{E_{0n} - E_{0k}} |\phi_{0k}\rangle + \cdots \quad (12)$$

first order

Have set $\lambda = 1$ in the above

Example

An infinite square well in 1D of width a has a potential "bump" at its centre, of height V' and covering one fifth of the width of the well. What is the first order effect on the eigenvalues?



Unperturbed system:

$$\phi_{0n}(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) \qquad E_{0n} = \frac{\hbar^2 \pi^2 n^2}{2ma^2}$$

First order perturbation:

$$E_{1n} = \frac{2}{a} \int_{0.4a}^{0.6a} \sin\left(\frac{n\pi x}{a}\right) V' \sin\left(\frac{n\pi x}{a}\right) dx$$

$$\therefore E_{1n} = V'\left(0.2 - \frac{\sin(1.2n\pi) - \sin(0.8n\pi)}{2n\pi}\right)$$

Energy of perturbed system (to first order)

$$E_n = E_{0n} + E_{1n}$$

For $n = 1$, $E_{11} = 0.39V'$ so energy of perturbed ground state

$$E_1 = \frac{\hbar^2\pi^2}{2ma^2} + 0.39V'$$

For $n = 2$, $E_{12} = 0.05V'$ so energy of perturbed first excited state

$$E_2 = \frac{2\hbar^2\pi^2}{ma^2} + 0.05V'$$

4.2 Degenerate perturbation theory

• If we look at equations (11) and (12) of section 4.1, we can see that problems will arise if the separation of unperturbed energy levels $E_{0n} - E_{0k}$ becomes smaller than $\langle \phi_{0k} | \hat{H}' | \phi_{0n} \rangle$.

e.g. 2nd order correction to E_n becomes large

• In particular, if two unperturbed eigenvalues are degenerate, the theory of section 4.1 fails completely.

• What effect does a perturbation have on two (or more) degenerate states?

- Consider the case of two degenerate states $|\phi_{01}\rangle$ and $|\phi_{02}\rangle$. These obey

TISE

$$\hat{H}_0|\phi_{01}\rangle = E_0|\phi_{01}\rangle \quad \text{and} \quad \hat{H}_0|\phi_{02}\rangle = E_0|\phi_{02}\rangle \qquad (1)$$

- We look for solutions of

$$\left(\hat{H}_0 + \hat{H}'\right)|\phi\rangle = E|\phi\rangle \qquad (2)$$

in the form

$$|\phi\rangle = a_1|\phi_{01}\rangle + a_2|\phi_{02}\rangle \qquad (3)$$

- Substitute (3) into (2) and use (1) to give

$$\left(E_0 - E\right)a_1|\phi_{01}\rangle + \left(E_0 - E\right)a_2|\phi_{02}\rangle$$
$$+ a_1\hat{H}'|\phi_{01}\rangle + a_2\hat{H}'|\phi_{02}\rangle = 0 \qquad (4)$$

Note that $|\phi_{01}\rangle$ and $|\phi_{02}\rangle$ are orthogonal and normalised, so $\langle\phi_{01}|\phi_{01}\rangle = 1$, $\langle\phi_{01}|\phi_{02}\rangle = 0$, etc

- Close (4) with $\langle \phi_{01} |$ and then $\langle \phi_{02} |$ to give

from closing with $\langle \phi_{01} |$

$$\left(E_0 + H'_{11} - E\right) a_1 + H'_{12}\, a_2 = 0 \qquad (5)$$

from closing with $\langle \phi_{02} |$

$$H'_{21}\, a_1 + \left(E_0 + H'_{22} - E\right) a_2 = 0 \qquad (6)$$

where $\quad H'_{\alpha\beta} = \langle \phi_{0\alpha} | \hat{H}' | \phi_{0\beta} \rangle \qquad (7)$

convenient shorthand

- (5) and (6) can be expressed in matrix form as

$$\begin{pmatrix} \left(E_0 + H'_{11}\right) - E & H'_{12} \\ H'_{21} & \left(E_0 + H'_{22}\right) - E \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} = 0$$

- Note that

$$H'_{21} = \left(H'_{12}\right)^* \quad (\hat{H}' \text{ is a Hermitian operator})$$

See problems sheets

This is a standard matrix eigenvalue problem. The eigenvalues E are determined by the condition

$$\begin{vmatrix} \left(E_0 + H'_{11}\right) - E & H'_{12} \\ H'_{21} & \left(E_0 + H'_{22}\right) - E \end{vmatrix} = 0 \qquad (9)$$

In the simple case where $H'_{11} = H'_{22}$ we get

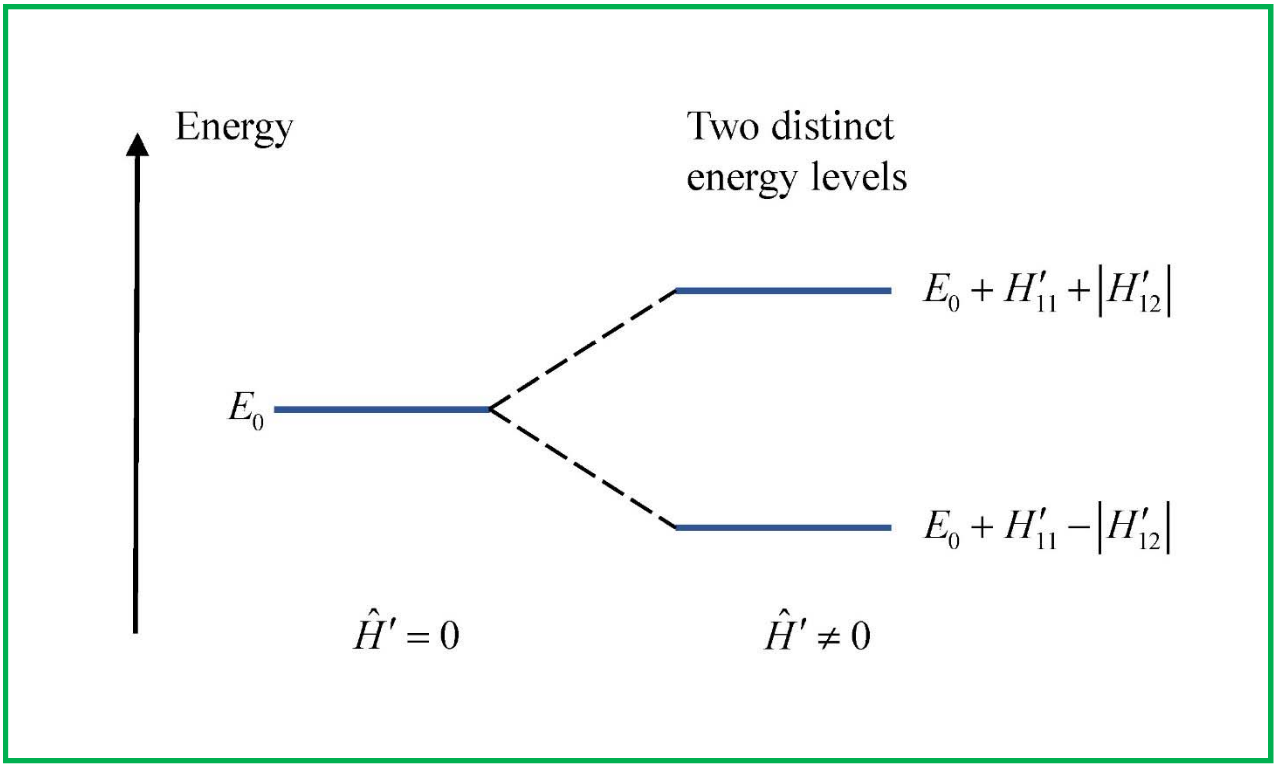
$$\left(\left(E_0 + H'_{11}\right) - E\right)^2 - \left|H'_{12}\right|^2 = 0$$

so

$$\boxed{E = E_0 + H'_{11} \pm \left|H'_{12}\right|} \qquad (10)$$

Two distinct energy levels

The perturbation breaks the degeneracy of $\left|\phi_{01}\right\rangle$ and $\left|\phi_{02}\right\rangle$


Energy
Two distinct
energy levels
$E_0 + H'_{11} + |H'_{12}|$
E_0
$E_0 + H'_{11} - |H'_{12}|$
$\hat{H}' = 0$
$\hat{H}' \neq 0$

The same method can be applied if there are M degenerate unperturbed states

Equation (3) is generalised to

$$\left|\phi\right\rangle = \sum_{m=1}^{M} a_m \left|\phi_{0m}\right\rangle$$

Equation (9) becomes

$$\boxed{\begin{vmatrix} H'_{11} - \Delta E & H'_{12} & \cdots & H'_{1M} \\ H'_{21} & H'_{22} - \Delta E & & \vdots \\ \vdots & & \ddots & \\ H'_{M1} & \cdots & & H'_{MM} - \Delta E \end{vmatrix} = 0 \qquad (11)}$$

$M \times M$ determinant – solve for M values of ΔE

where

$$H'_{\alpha\beta} = \left\langle \phi_{0\alpha} \middle| \hat{H}' \middle| \phi_{0\beta} \right\rangle$$

as above

and

$$\Delta E = E - E_0$$

Example: One dimensional "solid" of length L

$\boxed{V = 0}$

The unperturbed states will be free electron states in 1D:

$$|\phi_{0k}\rangle = \sqrt{\frac{1}{L}}\exp(ikx) \qquad E_{0k} = \frac{\hbar^2 k^2}{2m}$$

example of "box normalisation"

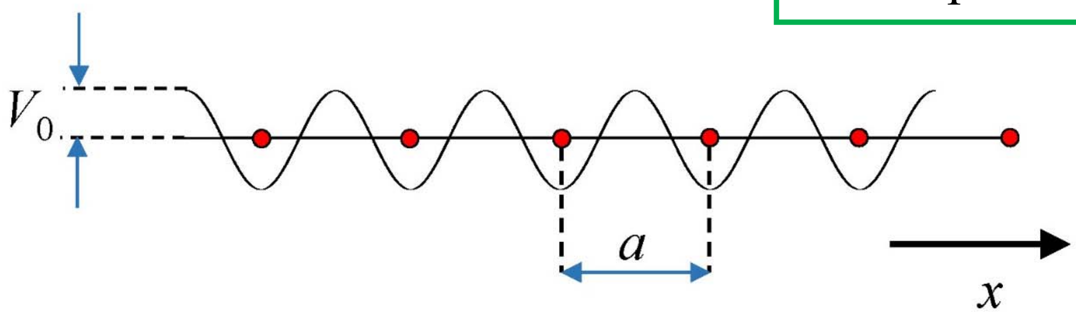
states $|\phi_{0k}\rangle$ and $|\phi_{0-k}\rangle$ have the same energy $\Rightarrow$ degenerate

The perturbation is a weak periodic potential:

$$\hat{H}' = V_0 \cos\left(\frac{2\pi x}{a}\right)$$

strength

repeat distance (ion core separation)



What happens to the eigenvalues?

'Nearly free electron model'

First calculate $H'_{\alpha\beta}$

See additional notes on 1D solid

$$H'_{kk} = H'_{k'k'} = \frac{V_0}{L}\int_0^L \cos\left(\frac{2\pi x}{a}\right) dx = 0 \qquad (12)$$

states are labelled by k

$$H'_{kk'} = \frac{1}{L}\int_0^L \exp(-ikx)\, V_0 \cos\left(\frac{2\pi x}{a}\right) \exp(ik'x)\, dx$$

$$\boxed{\begin{aligned} &= \frac{V_0}{2} \quad \text{if} \quad k - k' = \pm\frac{2\pi}{a} \\ &= 0 \quad \text{otherwise} \end{aligned}} \qquad (13)$$

$E_{0k} = \dfrac{\hbar^2 k^2}{2m}$ so the unperturbed state with $k = \dfrac{\pi}{a}$ is exactly degenerate with the state with $k' = -\dfrac{\pi}{a}$.

For these states, $k - k' = \dfrac{2\pi}{a}$ i.e. $H'_{kk'} = H'_{k'k} = \dfrac{V_0}{2}$

Equation (9) becomes

$$\begin{vmatrix} E_0 - E & V_0/2 \\ V_0/2 & E_0 - E \end{vmatrix} = 0$$

The solution is

$$\boxed{E = E_0 \pm V_0/2}$$

So the perturbation lifts the degeneracy of the electrons with $|k| = \dfrac{\pi}{a}$

We can extend our theory to nearly degenerate states, and consider unperturbed states with

$$k = \frac{\pi}{a} + \delta k \quad \text{call this } |\phi_{01}\rangle$$

$$k' = -\frac{\pi}{a} + \delta k \quad \text{call this } |\phi_{02}\rangle$$

The unperturbed energies of these states are

$$\boxed{\begin{array}{l} E_{0k} = \dfrac{\hbar^2 k^2}{2m} \\ \text{with} \\ k = \pm\dfrac{\pi}{a} + \delta k \end{array}}$$

$$E_{01} = \frac{\hbar^2}{2m}\left(\left(\frac{\pi}{a}\right)^2 + \delta k^2 + \frac{2\pi\,\delta k}{a}\right)$$

$$E_{02} = \underbrace{\frac{\hbar^2}{2m}\left(\left(\frac{\pi}{a}\right)^2 + \delta k^2\right.}_{\boxed{\bar{E}_0}}\left. - \frac{2\pi\,\delta k}{a}\right)$$

Write these as

$$E_{01} = \bar{E}_0 + \frac{\hbar^2 \pi\,\delta k}{ma} \quad \text{and} \quad E_{02} = \bar{E}_0 - \frac{\hbar^2 \pi\,\delta k}{ma}$$

From (12) and (13) we have

$$H'_{11} = H'_{22} = 0 \quad \text{and} \quad H'_{12} = H'_{21} = \frac{V_0}{2}$$

$$\boxed{H'_{kk} = H'_{k'k'} = 0} \qquad \boxed{H'_{kk'} = H'_{k'k} = V_0/2}$$

All the previous analysis goes through, and equation (9) becomes

$$\begin{vmatrix} \left(E_{01} + H'_{kk}\right) - E & H'_{kk'} \\ H'_{k'k} & \left(E_{02} + H'_{k'k'}\right) - E \end{vmatrix} = 0$$

or

$$\begin{vmatrix} \dfrac{\hbar^2 \pi \delta k}{ma} - \left(E - \bar{E}_0\right) & \dfrac{V_0}{2} \\ \dfrac{V_0}{2} & -\dfrac{\hbar^2 \pi \delta k}{ma} - \left(E - \bar{E}_0\right) \end{vmatrix} = 0$$

Solving this gives

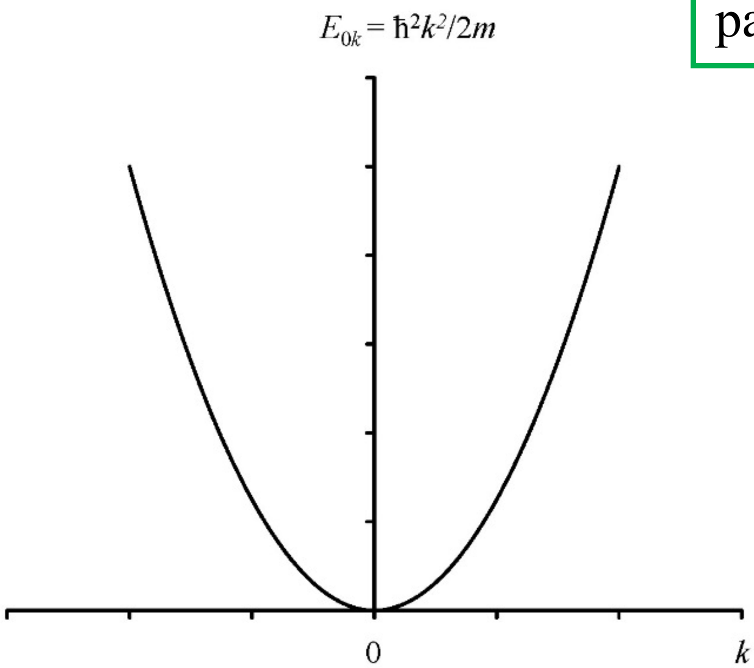
$$\boxed{E = \bar{E}_0 \pm \sqrt{\left(\frac{\hbar^2 \pi \delta k}{ma}\right)^2 + \frac{V_0^2}{4}}}$$

The perturbation affects states over a range of δk values where $\dfrac{\hbar^2 \pi\, \delta k}{ma}$ is small compared to $\dfrac{V_0}{2}$ i.e. perturbation has a negligible effect on states that are not close to $k = \pm\dfrac{\pi}{a}$ - see Rae

When $\delta k = 0$ there is a "band gap" of size V_0

Unperturbed system: -

Free electron parabola



Perturbed system: -

Band gap at Brillouin zone boundary