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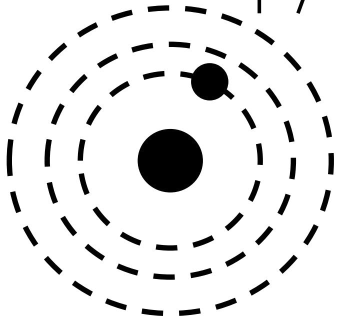
"Fides et Ratio"

Physics of Information Technology II
Physics of Molecular Bionics II
2014 Autumn

Lecture 6
Interactions
Collision-type, Sinusoidal type
Perturbation theory
Time-independent perturbation



$|i\rangle$

(i) Given an atom $\hat{H}_0|n\rangle = E_n|n\rangle$
prepared at a given time $t_0 = t_{initial}$
in a particular initial state $|i\rangle$
(ii) And the atom is subjected from this time onwards $t > t_0$ to an external interaction $\hat{H}_I(t)$

$$\hat{H} = \hat{H}_0 + H_I(t)$$

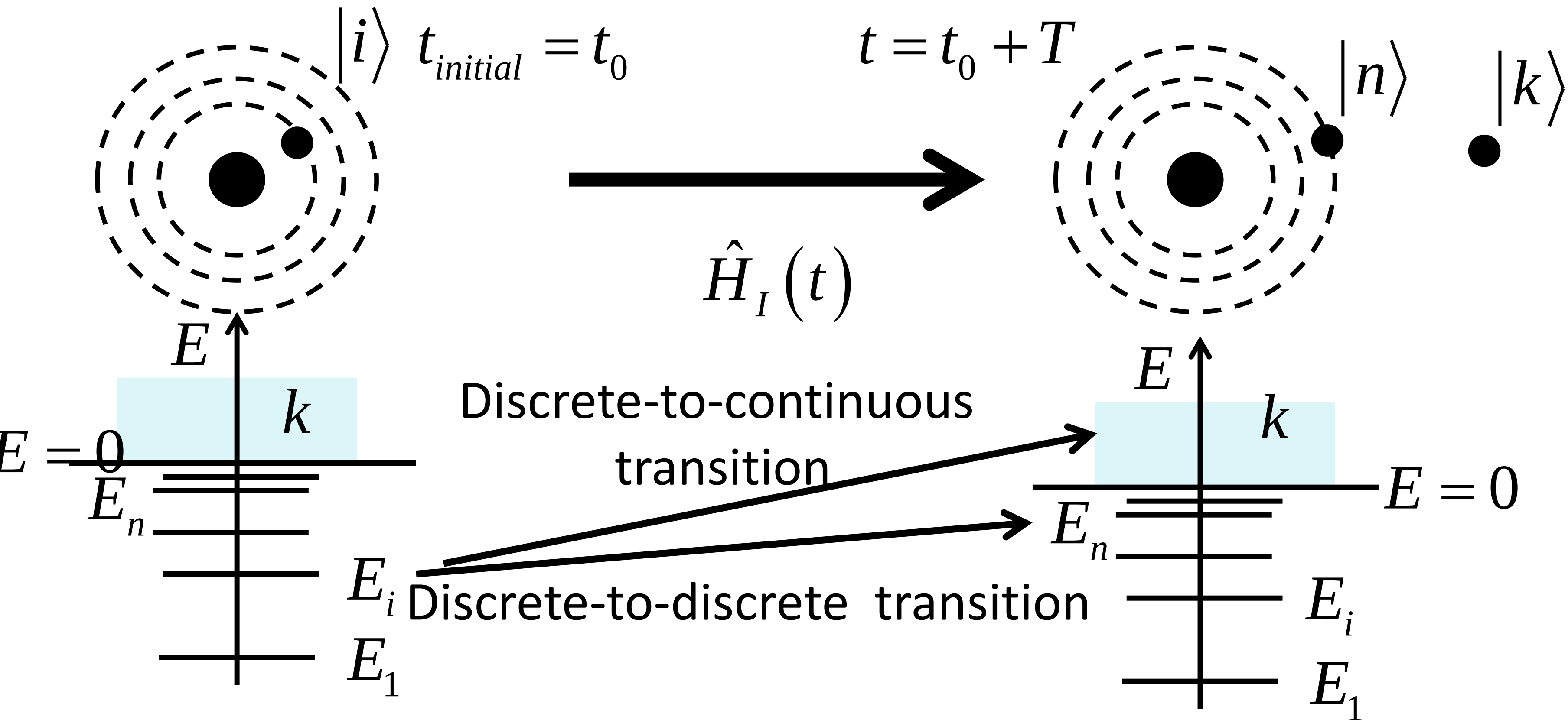
(iii) What state the atom is at any later moment of time?

(iv) What is the probability of finding the atom in another state at a time $t_0 + T$?

$$t = t_0 \rightarrow |\psi(t_0)\rangle = |i\rangle \qquad \forall t \rightarrow |\psi(t)\rangle = \sum_n c_n(t) e^{-j\frac{E_n}{\hbar}t}|n\rangle$$

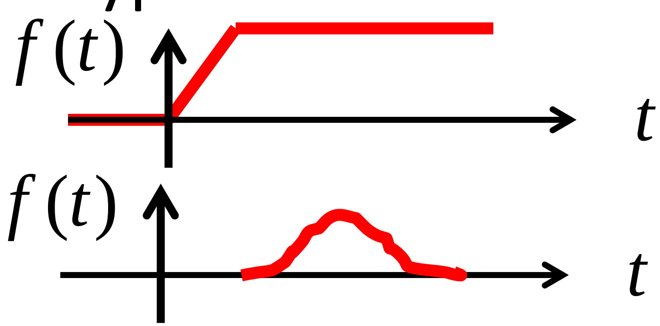
$$\mathrm{j}\hbar\frac{\mathrm{d}}{\mathrm{d}t}|\psi(t)\rangle = \left(\hat{H}_0 + \hat{H}_I(t)\right)|\psi(t)\rangle$$

$$t = t_0 + T \rightarrow P_{|i\rangle\rightarrow|n\rangle} = \left|c_n(t_0+T)\right|^2 = \left|\langle n|\psi(t_0+T)\rangle\right|^2$$

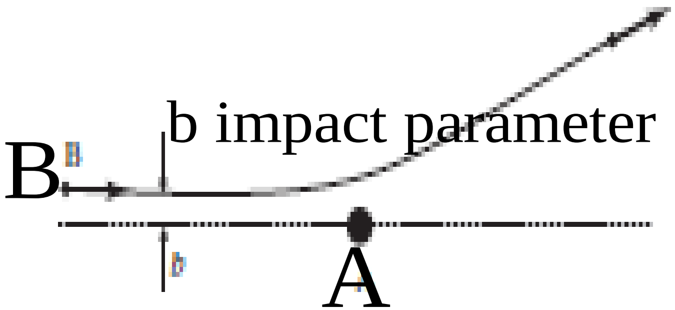


Collision-type transitions

$$\hat{H}_I(t) = \hat{W} \cdot f(t)$$



We consider a stationary atom "A", of which is described the hamiltonian $\hat{H}_0$, and we suppose that another particle "B" passes in the neighborhood of "A".



The interaction potential depends on the distance between A and B: $\hat{V}\left[R(t)\right]$, thus it depends on time. $\hat{V}\left[R(t)\right] = \hat{W}(R)\, f(t)$,

Before the collision the state of atom A is $|n\rangle$

There is a possibility that after the collision the state changes to $|m\rangle$

If the energies before and after the collision are the same:

ELASTIC COLLISION

Otherwise:

INELASTIC COLLISION

Sinusoidal -type interaction

An atom of $\hat{H}_0$ interacts with an incident classical electromagnetic wave of which the electric field at the position of the stationary atom is

$$\mathbf{E}(t) = \mathbf{E}\cos(\omega t + \varphi)$$

To a good approximation, the interaction of the atom and the field can be given in terms of electric dipole coupling $\hat{H}_I(t) = -\hat{\mathbf{D}} \cdot \mathbf{E}(t)$; where the electric dipole of the atom is $\hat{\mathbf{D}} = q\hat{\mathbf{r}}$ (Here q is the electric charge, and $\mathbf{r}$ the radius vector between the nucleus and its valence electron).

Perturbation Theory

$$\hat{H} = \hat{H}_0 + H_I(t) \qquad \hat{H}_0 |n\rangle = E_n |n\rangle$$

Weak interaction: $\langle n | H_I | m \rangle << |E_n - E_m|$

$$\hat{H}_I(t) = \lambda H_I^{'}(t);$$

$$\lambda << 1$$

λ is a real, diemnsionless parameter, much smaller than unity, which characterizes the relative strenghts of the interaction $\hat{H}_I(t)$

(In the two examples, λ is proportional (i) to the amplitude of the incident electric field, (ii) λ is a function of the impact parameter b)

$\lambda << 1$ is valid if the electric field is weak,
or the impact parameter is large.

Schrödinger equation: $$\mathrm{j}\hbar\frac{\mathrm{d}}{\mathrm{d}t}\left|\psi(t)\right\rangle=\left(\hat{H}_0+\lambda H_I^{'}(t)\right)\left|\psi(t)\right\rangle$$

Expanding $\left|\psi(t)\right\rangle$ in the basis of eigen-states of $\hat{H}_0$ we get

$$\left|\psi(t)\right\rangle=\sum_n c_n(t)e^{-\mathrm{j}\frac{E_n}{\hbar}t}\left|n\right\rangle$$

We project on the eigen-state $\left|k\right\rangle$ of $\hat{H}_0$, and use the identity $\sum_n\left|n\right\rangle\left\langle n\right|=1$

$$\mathrm{j}\hbar\frac{\mathrm{d}}{\mathrm{d}t}\left\langle k\middle|\psi(t)\right\rangle=\left\langle k\middle|\hat{H}_0\middle|\psi(t)\right\rangle+\lambda\left\langle k\middle|H_I^{'}(t)\middle|\psi(t)\right\rangle=$$

$$=E_k\left\langle k\middle|\psi(t)\right\rangle+\lambda\sum_n\left\langle k\middle|H_I^{'}(t)\middle|n\right\rangle c_n(t)e^{-\mathrm{j}\frac{E_n}{\hbar}t}$$

$$\left[E_k c_k(t)+\mathrm{j}\hbar\frac{\mathrm{d}}{\mathrm{d}t}c_k(t)\right]e^{-\mathrm{j}\frac{E_k}{\hbar}t}=E_k c_k(t)e^{-\mathrm{j}\frac{E_k}{\hbar}t}+\lambda\sum_n\left\langle k\middle|H_I^{'}(t)\middle|n\right\rangle c_n(t)e^{-\mathrm{j}\frac{E_n}{\hbar}t}$$

$$\mathrm{j}\hbar \frac{\mathrm{d}}{\mathrm{d}t} c_k(t) = \lambda \sum_n \langle k | H_I^{'}(t) | n \rangle e^{\mathrm{j}\frac{(E_k - E_n)}{\hbar} t} c_n(t)$$

No approximation having been made this far!

Possibly infinite system of ordinary differential equations

The coefficients $c_n(t)$ depend on λ

Perturbation theory consists of developing $c_n(t)$ as a power series of λ

$$c_k(t) = c_k^0(t) + \lambda c_k^1(t) + \lambda^2 c_k^2(t) + \dots$$

Substituting this series we can collect together the same order in λ

Oder 0
$$\mathrm{j}\hbar\frac{\mathrm{d}}{\mathrm{d}t}c_k^0(t)=0$$

Oder 1
$$\mathrm{j}\hbar\frac{\mathrm{d}}{\mathrm{d}t}c_k^1(t)=\lambda\sum_n\langle k|H_I^{'}(t)|n\rangle e^{\mathrm{j}\frac{(E_k-E_n)}{\hbar}t}c_n^0(t)$$

Oder *r*
$$\mathrm{j}\hbar\frac{\mathrm{d}}{\mathrm{d}t}c_k^r(t)=\lambda\sum_n\langle k|H_I^{'}(t)|n\rangle e^{\mathrm{j}\frac{(E_k-E_n)}{\hbar}t}c_n^{r-1}(t)$$

This system of equations can be solved iteratively. The zero order terms are already known: they are the constants determined by the initial state of the system . On substituting these terms, the first order solutions for $c_k^1(t);\ k=1,2,3,\ldots$ can be found. And so on.

Perturbation of the Stationary States

- Let us assume that the 'universe' is a closed quantum-mechanical system with known stationary eigenvalues and eigenstates

The stationary state Hamiltonian is $\hat{\mathbf{H}}_0$

$$\hat{\mathbf{H}}_0 \left|\psi_n^0\right\rangle = E_n^0 \left|\psi_n^0\right\rangle \quad \Rightarrow$$

$$E_1^0,\ E_2^0,\ \ldots,\ E_n^0,\ldots \quad \text{and} \quad \left|\psi_1^0\right\rangle, \left|\psi_2^0\right\rangle, \ldots, \left|\psi_n^0\right\rangle, \ldots,$$

and the external electromagnetic field is weak compared to the internal forces

$$\left(\hat{\mathbf{H}}_0 + \hat{\mathbf{H}}'\right)\left|\psi_n\right\rangle = \left(\hat{\mathbf{H}}_0 + \lambda\,\hat{\mathbf{V}}\right)\left|\psi_n\right\rangle = E_n\left|\psi_n\right\rangle.$$

The “perturbed” system
(stationary + weak electromagnetic field)

$$\left(\hat{\mathbf{H}}_0 + \hat{\mathbf{H}}'\right)\left|\psi_n\right\rangle = \left(\hat{\mathbf{H}}_0 + \lambda\,\hat{\mathbf{V}}\right)\left|\psi_n\right\rangle = E_n\left|\psi_n\right\rangle. \qquad 0<\lambda<1$$

$$\hat{\mathbf{H}}' = \lambda\hat{\mathbf{V}}, \quad \text{where} \quad \hat{\mathbf{H}}' \Rightarrow \hat{\mathbf{H}}_0, \text{ if } \quad \lambda \Rightarrow 0.$$

The perturbed problem is

$$\left(\hat{\mathbf{H}}_0 + \hat{\mathbf{H}}'\right)\left|\psi_n\right\rangle = \left(\hat{\mathbf{H}}_0 + \lambda\,\hat{\mathbf{V}}\right)\left|\psi_n\right\rangle = E_n\left|\psi_n\right\rangle.$$

If the perturbation operator does not depend on time, we call the problem ‘time-independent’ perturbation, if it does, ‘time-dependent’ perturbation.

Time-independent perturbation of stationary states

$$\left(\hat{\mathbf{H}}_0 + \hat{\mathbf{H}}'\right)\left|\psi_n\right\rangle = \left(\hat{\mathbf{H}}_0 + \lambda\hat{\mathbf{V}}\right)\left|\psi_n\right\rangle = E_n\left|\psi_n\right\rangle.$$

Let us expand the unknowns into a series of

$$\left|\psi\right\rangle = \left|\psi_0\right\rangle + \lambda\left|\psi_1\right\rangle + \lambda^2\left|\psi_2\right\rangle + \ldots;$$

$$E = E_0 + \lambda E_1 + \lambda^2 E_2 + \ldots;$$

$$\left(\hat{\mathbf{H}}_0 + \lambda\hat{\mathbf{V}}\right)\left(\left|\psi_0\right\rangle + \lambda\left|\psi_1\right\rangle + \lambda^2\left|\psi_2\right\rangle + \ldots,\right) =$$

$$= \left(E_0 + \lambda E_1 + \lambda^2 E_2 + \ldots,\right)\left(\left|\psi_0\right\rangle + \lambda\left|\psi_1\right\rangle + \lambda^2\left|\psi_2\right\rangle + \ldots,\right)$$

$$\mathbf{H}_0|\psi_0\rangle+\lambda\left(\hat{\mathbf{H}}_0|\psi_1\rangle+\hat{\mathbf{V}}|\psi_0\rangle\right)+\lambda^2\left(\hat{\mathbf{H}}_0|\psi_2\rangle+\hat{\mathbf{V}}|\psi_1\rangle\right)+\ldots=$$
$$=E_0|\psi_0\rangle+\lambda\left(E_0|\psi_1\rangle+E_1|\psi_0\rangle\right)+\lambda^2\left(E_0|\psi_2\rangle+E_1|\psi_1\rangle+E_2|\psi_0\rangle\right)+\ldots$$

$$\lambda^0 \quad \Rightarrow \quad \hat{\mathbf{H}}_0|\psi_0\rangle=E_0|\psi_0\rangle,$$
$$\lambda^1 \quad \Rightarrow \quad \hat{\mathbf{H}}_0|\psi_1\rangle+\hat{\mathbf{V}}|\psi_0\rangle=E_0|\psi_1\rangle+E_1|\psi_0\rangle,$$
$$\lambda^2 \quad \Rightarrow \quad \hat{\mathbf{H}}_0|\psi_2\rangle+\hat{\mathbf{V}}|\psi_1\rangle=E_0|\psi_2\rangle+E_1|\psi_1\rangle+E_2|\psi_0\rangle.$$

‘Zero-order’ approximation of the solution (the unperturbed)

$$E_0=E_m^0, \qquad |\psi_0\rangle=|m\rangle.$$

First order approximation of the solution

$$\sum_n E_n^0 |n\rangle\langle n|\psi_1\rangle + V|m\rangle = E_m^0 \sum_n |n\rangle\langle n|\psi_1\rangle + E_1|m\rangle.$$

Multiply it from left by 'ket' $\langle k|$

$$k \neq m \quad \Rightarrow \quad E_k^0 \langle k|\psi_1\rangle + \langle k|\hat{\mathbf{V}}|m\rangle = E_m^0 \langle \psi_k|\psi_1\rangle + E_1\delta_{km} \quad \Rightarrow$$

$$\boxed{E_0 = E_m^0 + \langle m|\hat{\mathbf{V}}|m\rangle = E_m^0 + V_{mm},}$$

$$|\psi\rangle = |m\rangle + \sum_{k\neq m} \frac{\langle k|\hat{\mathbf{V}}|m\rangle}{E_m^0 - E_k^0}|k\rangle.$$

‘Second-order’ approximation (mutatis mutandis)

$$E = E_m^0 + V_{mm} + \sum_{n \neq m} \frac{\left|V_{mn}\right|^2}{E_m^0 - E_n^0},$$

$$\left|\psi\right\rangle = \left|m\right\rangle + \sum_{k \neq m} \frac{V_{km}}{E_m^0 - E_k^0}\left|k\right\rangle +$$

$$+\sum_{k \neq m}\left[\sum_{n \neq m} \frac{V_{kn} V_{mn}}{\left(E_m^0 - E_n^0\right)\left(E_m^0 - E_k^0\right)} - \frac{V_{mm} V_{km}}{\left(E_m^0 - E_k^0\right)^2}\right]\left|k\right\rangle -$$

$$-\sum_{k \neq m} \frac{\left|V_{km}\right|^2}{2\left(E_m^0 - E_k^0\right)^2}\left|m\right\rangle.$$

In conclusion, first order approximation of perturbed eigenvalues and eigenstates:

$$E_1^0, \qquad E_1 = E_1^0 + \langle 1|\hat{\mathbf{V}}|1\rangle,$$

$$E_2^0, \qquad E_2 = E_2^0 + \langle 2|\hat{\mathbf{V}}|2\rangle,$$

$$E_3^0, \ldots, \qquad E_3 = E_3^0 + \langle 3|\hat{\mathbf{V}}|3\rangle, \ldots,$$

$$E_n^0, \ldots \qquad E_n = E_n^0 + \langle n|\hat{\mathbf{V}}|n\rangle, \ldots$$

$$|1\rangle, |2\rangle, |3\rangle, \ldots, |n\rangle, \ldots$$

$$|\psi_1\rangle = |1\rangle + \sum_{k\neq 1} \frac{\langle k|\hat{\mathbf{V}}|1\rangle}{E_1^0 - E_k^0}|k\rangle,$$

$$|\psi_2\rangle = |2\rangle + \sum_{k\neq 2} \frac{\langle k|\hat{\mathbf{V}}|2\rangle}{E_2^0 - E_k^0}|k\rangle,$$

$$|\psi_3\rangle = |3\rangle + \sum_{k\neq 3} \frac{\langle k|\hat{\mathbf{V}}|3\rangle}{E_3^0 - E_k^0}|k\rangle, \ldots$$

$$|\psi_n\rangle = |n\rangle + \sum_{k\neq n} \frac{\langle k|\hat{\mathbf{V}}|n\rangle}{E_n^0 - E_k^0}|k\rangle, \ldots$$

Start with the eigenvalues and the complete orthonormal set of eigenfunctions generated by the nonperturbed problem. The perturbation operator V is given. For the solution of a perturbation problem we have to calculate elements of the matrix

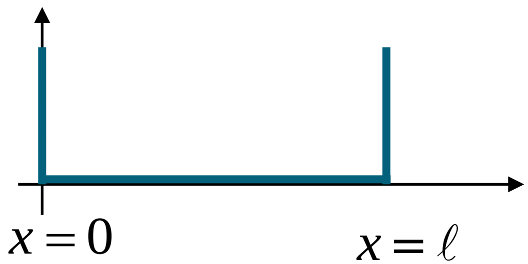
$$\begin{bmatrix} \langle 1|\hat{\mathbf{V}}|1\rangle & \langle 1|\hat{\mathbf{V}}|2\rangle & \langle 1|\hat{\mathbf{V}}|3\rangle & \cdots \\ \langle 2|\hat{\mathbf{V}}|1\rangle & \langle 2|\hat{\mathbf{V}}|2\rangle & \langle 2|\hat{\mathbf{V}}|3\rangle & \cdots \\ \langle 3|\hat{\mathbf{V}}|1\rangle & \langle 3|\hat{\mathbf{V}}|2\rangle & \langle 3|\hat{\mathbf{V}}|3\rangle & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix}.$$

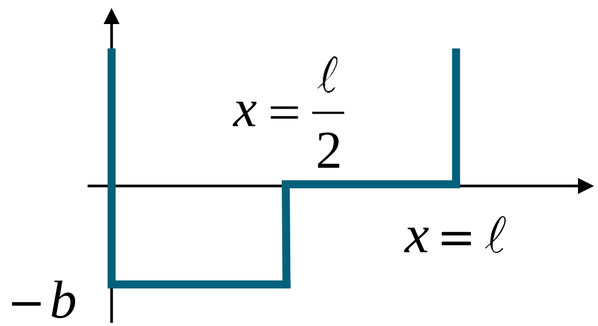
Every element is an integral on the configuration space

$$\langle n|\hat{\mathbf{V}}|m\rangle = \int_{\text{Conf .space}} \psi_n^* \hat{\mathbf{V}} \psi_m \mathrm{d}q_1 \ldots \mathrm{d}q_f \, .$$

Example 1: A particle moves in a one-dimensional potential box with a small potential dip.

- Treat the potential dip as a perturbation to a regular box. Find the first order approach of the energy of the ground state.





$$V_{\text{pot}} = \begin{cases} \infty & \text{for} \quad x < 0, \text{ and } x > \ell \\ 0 & \text{for} \quad 0 < x < \ell \end{cases}$$

$$V'_{\text{pot}} = \begin{cases} \infty & \text{for} \quad x < 0, \text{ and } x > \ell \\ -b & \text{for} \quad 0 < x < \ell/2 \\ 0 & \text{for} \quad \ell/2 < x < \ell \end{cases}$$

$$E_n^0 = \frac{h^2}{8m\ell^2} n^2; \quad \psi_n^0(x) = \sqrt{\frac{2}{\ell}} \sin \frac{n\pi}{\ell} x$$

The first order approach of the energy of the ground

$$E_0 - E_0^0 = \langle 1|\mathbf{V}|1\rangle = \int_{-\infty}^{+\infty} \psi_0^{0*}(x)\mathbf{V}(x)\psi_0^0(x)\mathrm{d}x =$$

$$= \int_0^{\ell/2} \psi_0^{0*}(x)\left(-b\right)\psi_0^0(x)\,\mathrm{d}x = \int_0^{\ell/2} \frac{2}{\ell}\sin^2\left(\frac{\pi x}{\ell}\right)\left(-b\right)\mathrm{d}x =$$

$$= \int_0^{\ell/2} \frac{2}{\ell}\sin^2\left(\frac{\pi x}{\ell}\right)\left(-b\right)\mathrm{d}x = -\frac{b}{\ell}\int_0^{\ell/2}\left(1-\cos\frac{2\pi x}{\ell}\right)\mathrm{d}x,$$

$$E_0 = E_0^0 + \langle 1|\mathbf{V}|1\rangle = \frac{\mathrm{h}^2}{8m\ell^2} - \frac{b}{2}.$$

Problems

1. An electron is confined in the ground state in a one dimensional box of $a = 0.1\,\text{nm}$

a. Calculate the ground state and the first excited state energy of the electron.

b. Calculate the average force on the walls of the box when the electron is in the ground state.

$$E_n = \frac{h^2}{8ma^2} n^2 \quad n = 1, 2, \ldots$$

$$E_1 = 38\,\text{eV}; \quad E_2 = 4E_1 = 152\,\text{eV};$$

$$F = -\left\langle \partial \mathbf{H} / \partial a \right\rangle; \quad \mathbf{H}\psi_n = E_n \psi_n$$

$$\mathbf{H}-E_n \quad \psi_n = 0 \rightarrow \frac{\partial}{\partial a}\left[\ \mathbf{H}-E_n \quad \psi_n\right] =$$

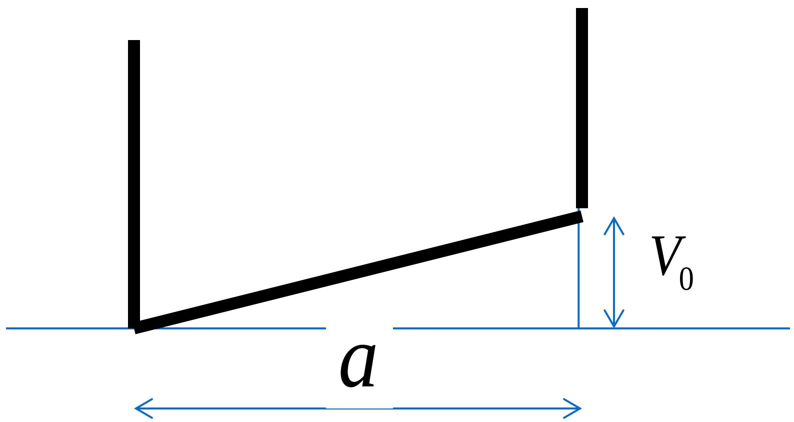
$$= \left(\frac{\partial}{\partial a}\mathbf{H} - \frac{\partial}{\partial a}E_n\right)\psi_n + \ \mathbf{H}-E_n \quad \frac{\partial}{\partial a}\psi_n = 0$$

$$\int \ \psi_n^* \left(\frac{\partial}{\partial a}\mathbf{H} - \frac{\partial}{\partial a}E_n\right)\psi_n \mathrm{d}x + \int \ \psi_n^* \ \ \mathbf{H}-E_n \quad \frac{\partial}{\partial a}\psi_n dx = 0$$

$$\left\langle \partial \mathbf{H} / \partial a \right\rangle = \partial E_n / \partial a \rightarrow F = -\partial E_n / \partial a$$

$$F = 2E_1 / a = 7.6 \cdot 10^{11} \text{ eV/m} = 760 \text{ eV/nm}$$

2. Applying first order perturbation theory, calculate the energy of the first three states for a one-dimensional potential box of width a, which has been perturbed with a linear potential according to the figure. Calculate the perturbed ground-state energy and the ground-state eigen-function.



3. A charged particle is bound in a harmonic oscillator of potential $\frac{1}{2}kx^2$. The system is placed into a static external electric field E.

Calculate the shift of the energy of the ground state up to order two.