PHYS-C0252 - Quantum Mechanics Part 9
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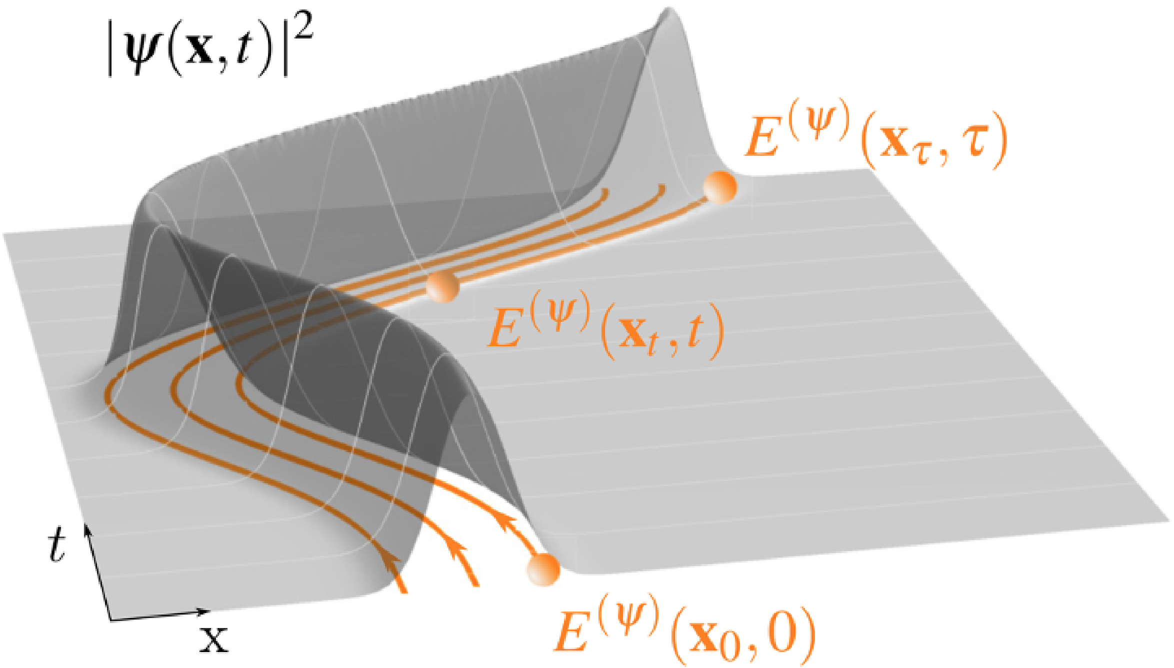


6. Perturbation Theory

6.1 Gram-Schmidt Orthogonalization

- Assume that we have a complete set of *linearly independent* eigenvectors that span a vector space (or Hilbert space), but they are not orthonormal.

- Assume for simplicity that the set is given by

$$S = \{|v_1\rangle, |v_2\rangle, ..., |v_n\rangle\}$$

and we want to create a new orthogonal set

$$S_\perp = \{|u_1\rangle, |u_2\rangle, ..., |u_n\rangle\}$$

that spans the same space as *S*

This is called the *Gram-Schmidt* process

- Define a projection operator

$$\hat{P}_u(v) \equiv \frac{\langle u|v\rangle}{\langle u|u\rangle}|u\rangle$$

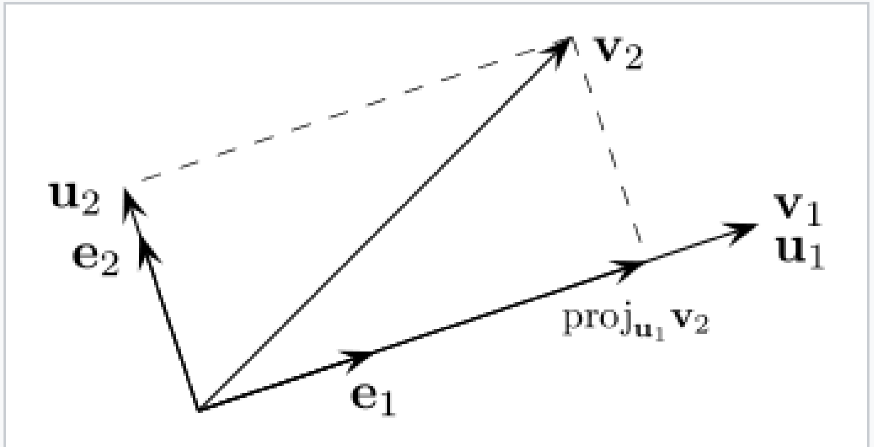
The GS process simply comprises repeated orthogonal projections, subtracting the non-orthogonal parts and finally normalizing:

$$|u_1\rangle = |v_1\rangle,\ |e_1\rangle = \frac{|u_1\rangle}{||u_1||}$$

$$|u_2\rangle = |v_2\rangle - \hat{P}_{u_1}(v_2),\ |e_2\rangle = \frac{|u_2\rangle}{||u_2||}$$

$$|u_3\rangle = |v_3\rangle - \hat{P}_{u_1}(v_3) - \hat{P}_{u_2}(v_3),\ \ |e_3\rangle = \frac{|u_3\rangle}{||u_3||}$$

$$|u_4\rangle = |v_4\rangle - \hat{P}_{u_1}(v_4) - \hat{P}_{u_2}(v_4) - \hat{P}_{u_3}(v_4),\ \ |e_4\rangle = \frac{|u_4\rangle}{||u_4||}$$



The first two steps of the Gram–Schmidt process

The final orthonormal basis set is thus

$$S_{\perp}^{\mathrm{N}} = \{|e_1\rangle, |e_2\rangle, ..., |e_n\rangle\}$$

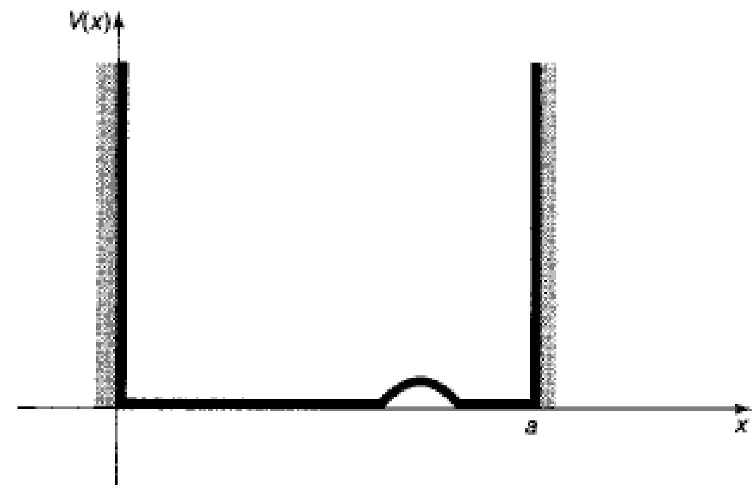
6.2 Time-Independent Perturbation Theory

- Assume that we have solved the SE for a given external potential such that

$$\hat{H}^0 \psi_n^0 = E_n^0 \psi_n^0$$

and the energy eigenfunctions form an orthonormal set

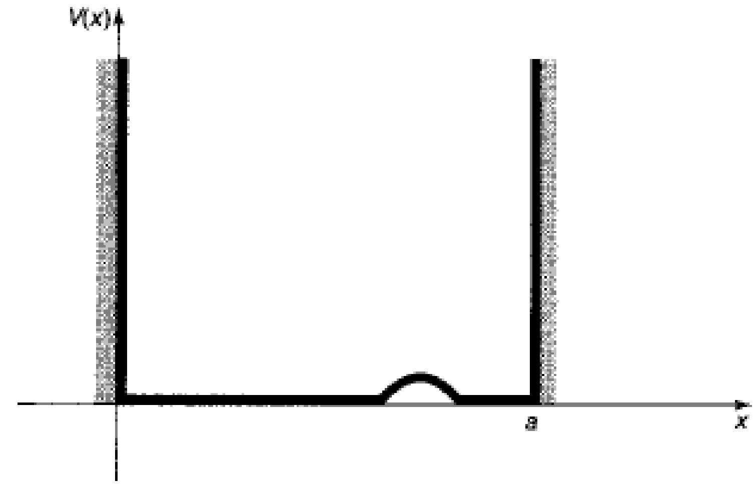
$$\langle \psi_n^0 | \psi_m^0 \rangle = \delta_{nm}$$



"Small" perturbation on *V*(*x*)

- If we could solve this new problem exactly

$$\hat{H}\psi_0 = E_n\psi_n$$



If however the perturbation is "small", we could try writing

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

where now $\lambda \ll 1$ such that we can (formally) expand

$$\psi_n = \psi_n^0 + \lambda\psi_n^1 + \lambda^2\psi_n^2 + ...$$

$$E_n = E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + ...$$

where the superscripts denote the *nth order corrections* to the unperturbed state denoted by 0

This expression is inserted into the modified SE to get

$$H^0\psi_n^0 + \lambda(H^0\psi_n^1 + H'\psi_n^0) + \lambda^2(H^0\psi_n^2 + H'\psi_n^1) + \cdots$$

$$= E_n^0\psi_n^0 + \lambda(E_n^0\psi_n^1 + E_n^1\psi_n^0) + \lambda^2(E_n^0\psi_n^2 + E_n^1\psi_n^1 + E_n^2\psi_n^0) + \cdots.$$

To lower order this gives just the unmodified SE. To first order

$$H^0\psi_n^1 + H'\psi_n^0 = E_n^0\psi_n^1 + E_n^1\psi_n^0$$

and to second order

$$H^0\psi_n^2 + H'\psi_n^1 = E_n^0\psi_n^2 + E_n^1\psi_n^1 + E_n^2\psi_n^0$$

Taking the inner product of the first equation with ψ_n^0 gives the first-order correction as

$$\boxed{E_n^1 = \langle\psi_n^0|H'|\psi_n^0\rangle.}$$

Rewriting the lowest order correction as

$$(H^0 - E_n^0)\psi_n^1 = -(H' - E_n^1)\psi_n^0.$$

and expanding the first-order correction in the original SE basis gives

$$\sum_{m\neq n}(E_m^0 - E_n^0)c_m^{(n)}\psi_m^0 = -(H' - E_n^1)\psi_n^0.$$

Taking the inner product with ψ_l^0

$$\sum_{m\neq n}(E_m^0 - E_n^0)c_m^{(n)}\langle\psi_l^0|\psi_m^0\rangle = -\langle\psi_l^0|H'|\psi_n^0\rangle + E_n^1\langle\psi_l^0|\psi_n^0\rangle.$$

and orthogonality gives

$$c_m^{(n)} = \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{E_n^0 - E_m^0}$$

which gives the first-order correction to the original SE basis as

$$\boxed{\psi_n^1 = \sum_{m \neq n} \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{(E_n^0 - E_m^0)} \psi_m^0.}$$

To get the second-order corrections, we use the second-order equation and operate with ψ_n^0

$$\langle\psi_n^0|H^0\psi_n^2\rangle + \langle\psi_n^0|H'\psi_n^1\rangle = E_n^0\langle\psi_n^0|\psi_n^2\rangle + E_n^1\langle\psi_n^0|\psi_n^1\rangle + E_n^2\langle\psi_n^0|\psi_n^0\rangle$$

where

$$\langle\psi_n^0|\psi_n^1\rangle = \sum_{m\neq n} c_m^{(n)}\langle\psi_n^0|\psi_m^0\rangle = 0$$

and thus

$$E_n^2 = \sum_{m\neq n} \frac{|\langle\psi_m^0|H'|\psi_n^0\rangle|^2}{E_n^0 - E_m^0}.$$

In degenerate case a general expansion in terms of eigenvectors of the original SE should be used