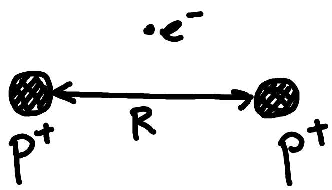
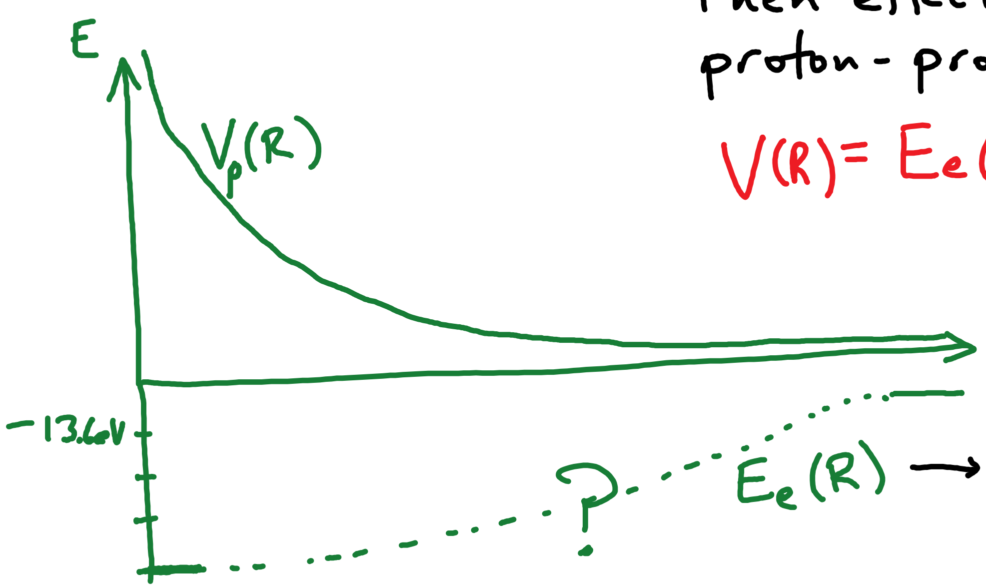
Another example: Hydrogen molecule ion



Use BORN-OPPENHEIMER approximation:

- compared to electron, protons are heavy + slow.
- treat these as classical, at some fixed R + solve QM problem for electron in this potential to get $E_e(R)$
- Then effective potential for proton-proton system is

$$V(R) = E_e(R) + \underbrace{\frac{1}{4\pi\varepsilon_0}\frac{e^2}{R}}_{V_p(R)}$$



$\rightarrow$ is there a minimum if we add this to $V(R)$?

Use variational method to show that for some R,

$$E_e(R) + V_p(R) < E_e(\infty) + V_p(\infty) = -13.6\,eV$$

Trial wavefunction: $\psi(\vec{x}) = A\left[\psi^1_{100}(\vec{x}) + \psi^2_{100}(\vec{x})\right]$

$\rightarrow$ superposition of ground states for two protons

LCAO "Linear combination of atomic orbitals"

TIME DEPENDENT PERTURBATION THEORY

→ Consider time indep system with Hamiltonian H_0, initially in some state $|\psi(0)\rangle$ at $t=0$

→ Now: turn on small time dep perturbation $H'(t)$ at $t=0$.

→ Want to know state at time t

TIME DEP S.E.:

$$i\hbar \frac{\partial}{\partial t}|\psi(t)\rangle = H_0|\psi(t)\rangle + H'(t)|\psi(t)\rangle$$

Define $|\psi_n\rangle \longrightarrow$ eigenstates of H_0 with energies E_n

$$|\psi(t)\rangle = \sum c_n(t)\, e^{-iE_nt/\hbar}|\psi_n\rangle$$

constant if $H'=0$

Plug in to S.E.

$$\sum i\hbar \dot{c}_n e^{-iE_nt/\hbar}|\psi_n\rangle + E_n c_n e^{-iE_nt/\hbar}|\psi_n\rangle$$

$$= \sum E_n c_n e^{-iE_nt/\hbar}|\psi_n\rangle + \sum c_n e^{-iE_nt/\hbar} H'(t)|\psi_n\rangle$$

$$\times\langle\psi_m| \Rightarrow \quad i\hbar \dot{c}_m e^{-iE_mt/\hbar} = \sum c_n e^{-iE_nt/\hbar}\langle\psi_m|H'(t)|\psi_n\rangle$$

$$\Rightarrow \boxed{\dot{c}_m(t) = -\frac{i}{\hbar}\sum_n e^{i(E_m-E_n)t/\hbar} H'_{mn}(t)\, c_n(t)}$$

$$H'_{mn} = \langle \psi_m | H'(t) | \psi_n \rangle \qquad \text{NO APPROXIMATION YET.}$$

$$\boxed{\dot{c}_m(t) = -\frac{i}{\hbar}\sum_n e^{i(E_m-E_n)t/\hbar} H'_{mn}(t)\; c_n(t)}$$

$H'_{mn}(t) = \langle\psi_m|H'(t)|\psi_n\rangle$

$$\dot{\vec{c}}(t) = \mathcal{M}(t)\,\vec{c}(t)$$

SOLUTION:

$$\vec{c}(t) = \vec{c}(0) + \underbrace{\vec{c}_1(t)}_{\mathcal{O}(\mathcal{M})}$$

$$\dot{\vec{c}}_1(t) = \mathcal{M}(t)\,\vec{c}(0) + \mathcal{M}(t)\,\vec{c}_1(t)$$

$$\Rightarrow \vec{c}_1(t) = \int_0^t M(t')dt' \cdot \vec{c}(0) + \mathcal{O}(M^2)$$

$$c_m(t) = c_m(0) - \frac{i}{\hbar}\sum_n \left[\int_0^t dt' e^{i(E_m-E_n)t'/\hbar} H'_{mn}(t')\right] c_n(0) + \mathcal{O}(H'^2)$$

APPLICATION: TRANSITION PROBABILITIES

→ Suppose we have an energy eigenstate at $t=0$

$$|\psi(0)\rangle = |\psi_a\rangle \qquad c_a(0) = 1 \quad c_m(0) = 0 \quad m \neq a.$$

→ Probability of finding state $|\psi_b\rangle$ at time t:

$$P_b(t) = |c_b(t)|^2 \approx \frac{1}{\hbar^2}\left|\int_0^t dt_1\, e^{i\omega_{ba}t_1} H'_{ba}(t_1)\right|^2$$

$$\omega_{ba} = (E_b - E_a)/\hbar$$

Total probability of making a transition

$$P_{tot} = \sum_{b\neq a} |c_b(t)|^2$$