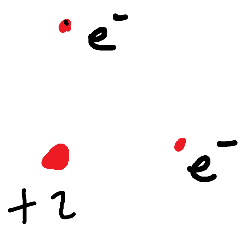
LAST TIME: Variational method

Q: Which of the following is true about the ground state energy of helium?



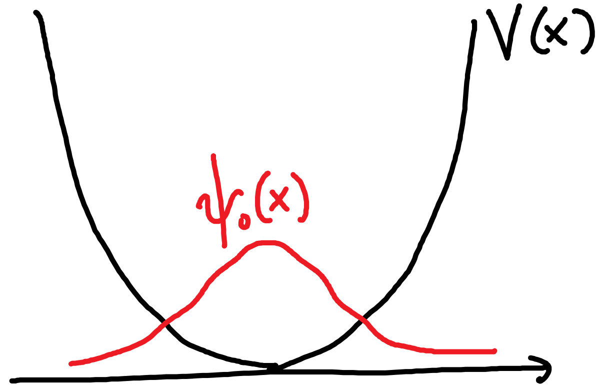
① $E_0 = -2 \times (13.6\,eV \times 4)$

② $E_0 > -2 \times (13.6\,eV \times 4)$

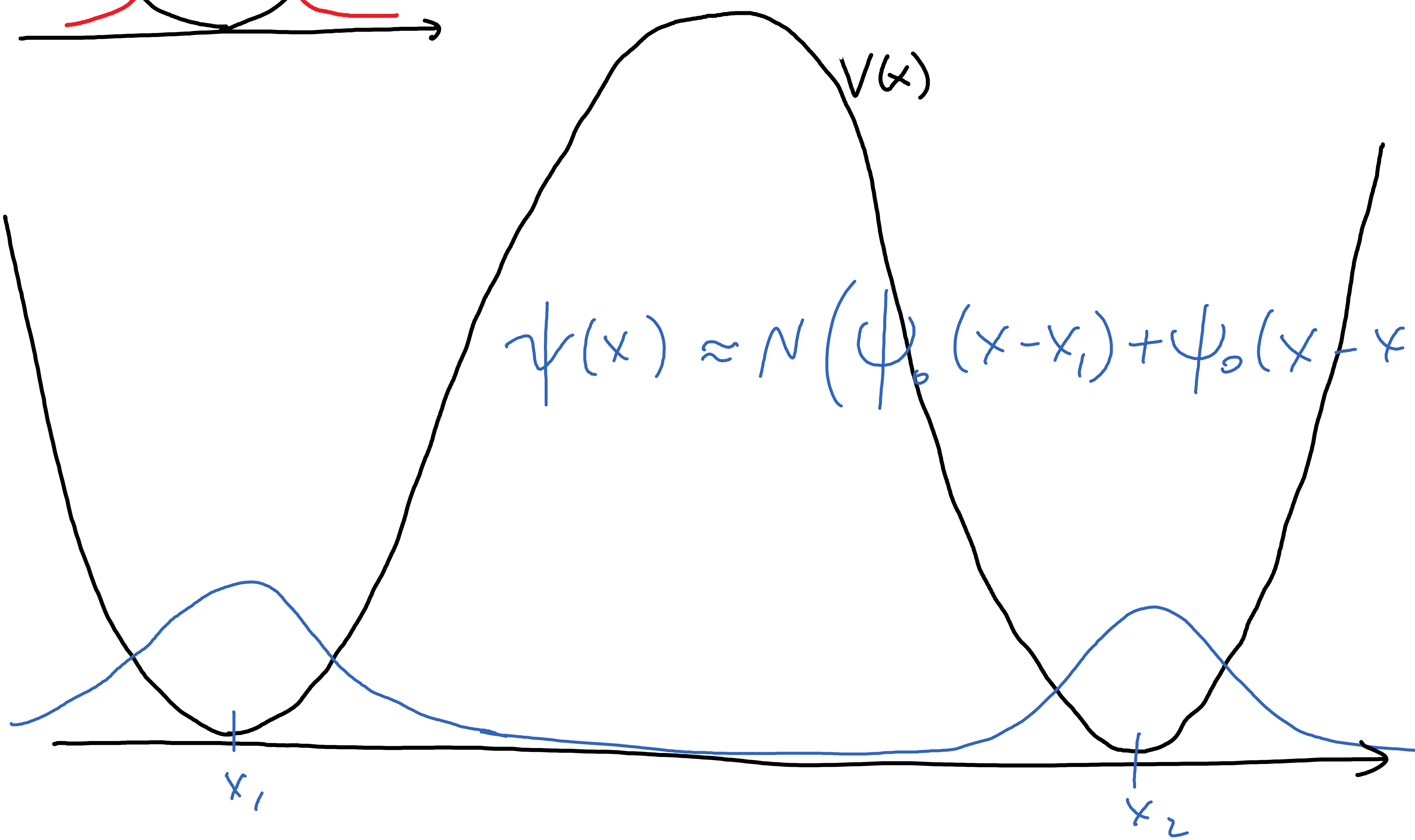
③ $E_0 < -2 \times (13.6\,eV \times 4)$

interaction gives potential

$$\frac{e^2}{4\pi\varepsilon_0} \frac{1}{|\vec{x}_1 - \vec{x}_2|} = \text{additional positive energy}$$



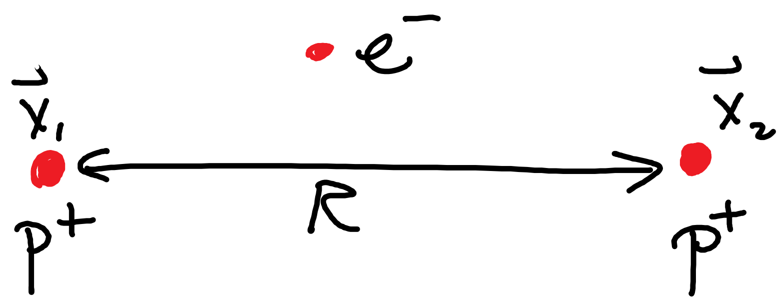
Q: The picture at the left shows the ground state wavefunction for a Harmonic oscillator potential. What do you think the ground state wavefunction looks like for the potential below?



$$\psi(x) \approx N\left(\psi_0(x - x_1) + \psi_0(x - x_2)\right)$$

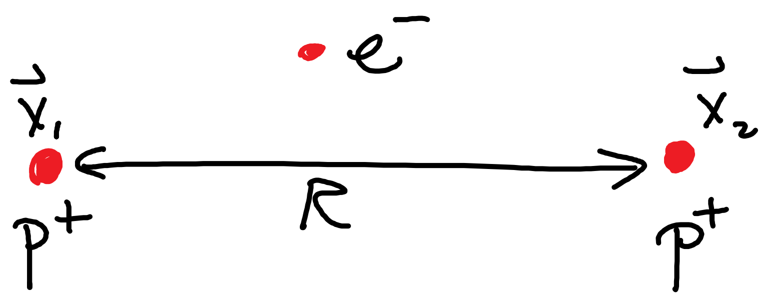
VARIATIONAL METHOD example: the hydrogen molecule ion

Is there a bound state?



VARIATIONAL METHOD example: the hydrogen molecule ion

Is there a bound state?



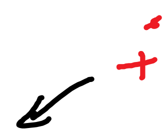
Useful quantity: $E_e^0(R)$: minimum electron energy for fixed R

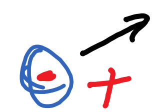
Q: What is $E_e^0(R)$ for $R \to 0$ and $R \to \infty$

(discussion)

$-13.6\,eV \times 4$

(This is He +)



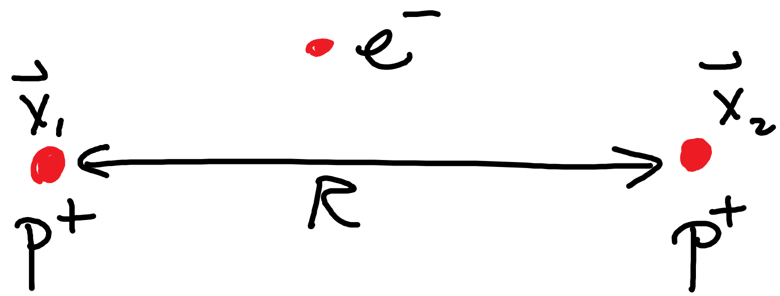


$-13.6\,eV$

H atom

+ proton

VARIATIONAL METHOD example: the hydrogen molecule ion



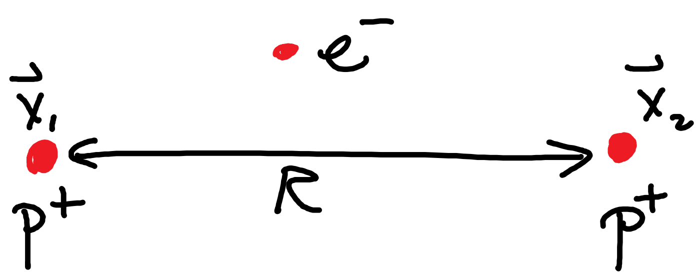
Is there a bound state?

① Consider fixed R, use trial wavefunction

$$\psi_{100}(\vec{x}-\vec{x}_1) + \psi_{100}(\vec{x}-\vec{x}_2)$$

to put upper bound $E_e^{var}(R)$ on $E_e^{0}(R)$

VARIATIONAL METHOD example: the hydrogen molecule ion



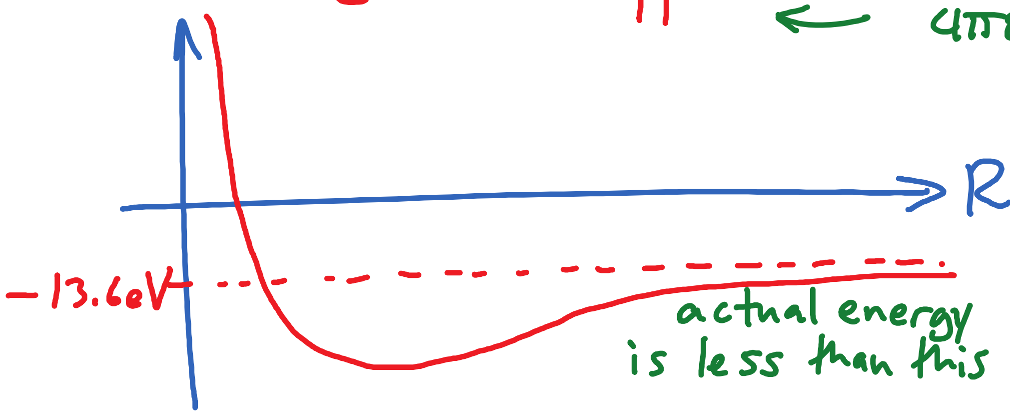
Is there a bound state?

① Consider fixed R, use trial wavefunction

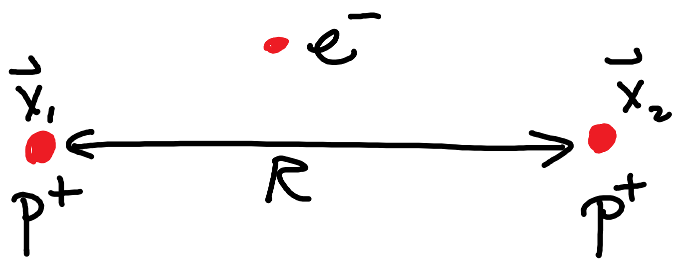
$$\psi_{100}(\vec{x}-\vec{x}_1)+\psi_{100}(\vec{x}-\vec{x}_2)$$

to put upper bound $E_e^{var}(R)$ on ground state electron energy.

② Consider $E_e^{var}(R)+V_{pp}(R) \leftarrow \frac{1}{4\pi\varepsilon_0}\frac{e^2}{R}$



VARIATIONAL METHOD example: the hydrogen molecule ion



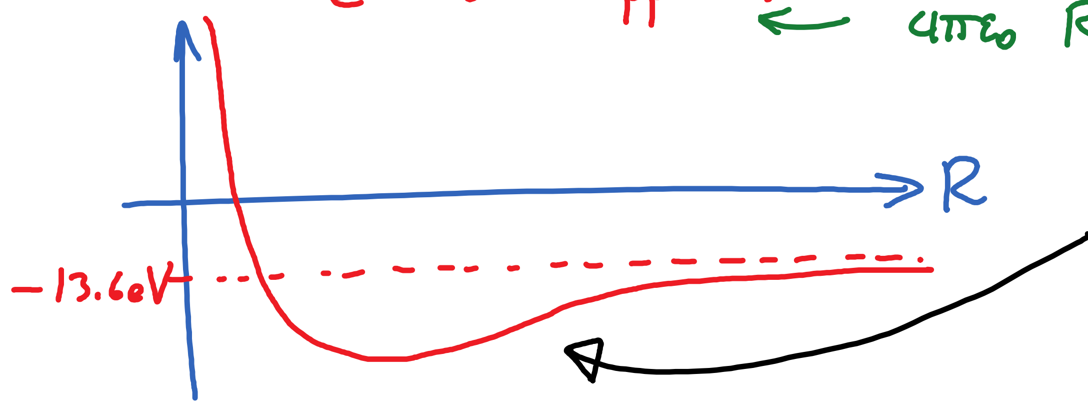
Is there a bound state?

① Consider fixed R, use trial wavefunction

$$\psi_{100}(\vec{x}-\vec{x}_1) + \psi_{100}(\vec{x}-\vec{x}_2)$$

to put upper bound $E_e^{var}(R)$ on ground state electron energy.

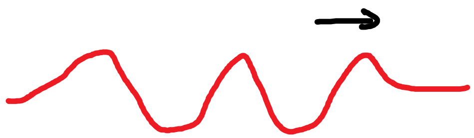
② Consider $E_e^{var}(R) + V_{pp}(R) \leftarrow \frac{1}{4\pi\varepsilon_0}\frac{e^2}{R}$



This is $< -13.6eV$ for some range of R, so there is a bound state

Time-Dependent Perturbation Theory

Before:

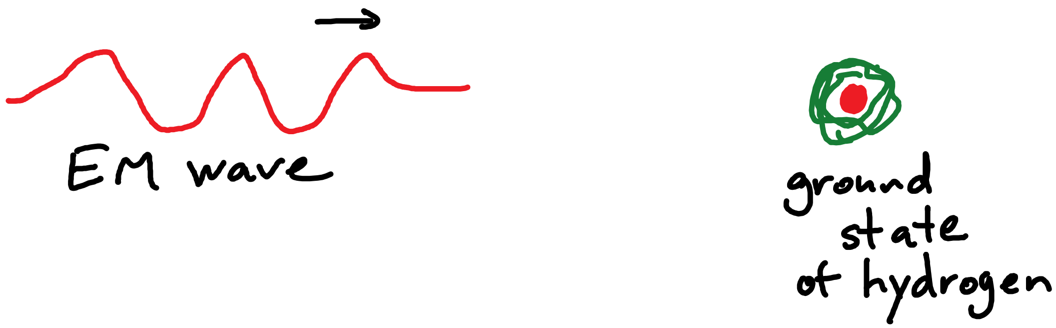


EM wave

ground state of hydrogen

TIME-DEPENDENT PERTURBATION THEORY

BEFORE:



An electromagnetic wave interacts with a hydrogen atom in its ground state. After the wave passes, we expect that:

1. The electron will still be in its ground state
2. The electron will be in one of its excited states
3. The electron will have left the atom
4. The electron will be in a superposition of some of the above possibilities

General problem: $H = H_0 + H'(t)$ ← nonzero for $t > 0$

Initial state: $|\Psi(0)\rangle = \sum c_n |\psi_n\rangle$ ← energy eigenstates of H_0

Want to approximate state at time t for small H'

Q: What is $|\Psi(t)\rangle$ if $H' = 0$?

General problem: $H = H_0 + H'(t)$ ← nonzero for $t > 0$

Initial state: $|\Psi(0)\rangle = \sum c_n |\psi_n\rangle$

← energy eigenstates of H_0 w. energy E_n

Want to approximate state at time t for small H'

Q: What is $|\Psi(t)\rangle$ if $H' = 0$?

A: $|\Psi(t)\rangle = \sum c_n e^{-iE_n t/\hbar} |\psi_n\rangle$

General problem: $H = H_0 + H'(t)$ ← nonzero for $t > 0$

Initial state: $|\Psi(0)\rangle = \sum c_n |\psi_n\rangle$

energy eigenstates of H_0 w. energy E_n

Want to approximate state at time t for small H'

Q: What is $|\Psi(t)\rangle$ if $H' = 0$?

A: $$|\Psi(t)\rangle = \sum_n c_n e^{-iE_n t/\hbar} |\psi_n\rangle$$

With $H'(t)$: $$|\Psi(t)\rangle = \sum_n c_n(t) e^{-iE_n t/\hbar} |\psi_n\rangle$$

want to find this

Reading question: Schrödinger equation gives:

$$\frac{dc_m}{dt} = -\frac{i}{\hbar}\sum_n e^{i(E_m-E_n)t/\hbar} H'_{mn}(t)\, c_n(t)$$

$$\langle \psi_m | H'(t) | \psi_n \rangle$$

Reading question: Schrödinger equation gives:

$$\frac{dc_m}{dt} = -\frac{i}{\hbar}\sum_n e^{i(E_m-E_n)t/\hbar} \underbrace{H'_{mn}(t)}_{\langle\psi_m|H'(t)|\psi_n\rangle} c_n(t)$$

Simpler version: $\frac{dc}{dt} = \underbrace{\varepsilon}_{\text{small}} \cdot f(t) \cdot c$

Q: Given $c(0)$, what is $c(t)$ for $\varepsilon = 0$?

Reading question: Schrödinger equation gives:

$$\frac{dc_m}{dt} = -\frac{i}{\hbar}\sum_n e^{i(E_m-E_n)t/\hbar} \underbrace{H'_{mn}(t)}_{\langle\psi_m|H'(t)|\psi_n\rangle} c_n(t)$$

Simpler version: $\frac{dc}{dt} = \underbrace{\varepsilon}_{\text{small}} \cdot f(t) \cdot c$

Q: Given $c(0)$, what is $c(t)$ for $\varepsilon = 0$?

A: For $\varepsilon = 0$, get $\frac{dc}{dt} = 0$ so $c(t) = c(0)$

PERTURBATION THEORY: $c(t) = c(0) + \varepsilon c_1(t) + \varepsilon^2 c_2(t) + \ldots$

Simpler version: $\dfrac{dc}{dt} = \underset{\text{small}}{\varepsilon} \cdot f(t) \cdot c$

PERTURBATION THEORY: $c(t) = c(0) + \varepsilon c_1(t) + \varepsilon^2 c_2(t) + \cdots$

Discussion questions:

A) Derive an equation for $c_1(t)$

B) Solve this equation (given $c(0)$)

Simpler version: $\dfrac{dc}{dt} = \underbrace{\varepsilon}_{\text{small}} \cdot f(t) \cdot c$

PERTURBATION THEORY: $c(t) = c(0) + \varepsilon c_1(t) + \varepsilon^2 c_2(t) + \dots$

A) Derive an equation for $c_1(t)$

$$\frac{d}{dt}\left[c(0) + \varepsilon c_1(t) + \varepsilon^2 c_2(t) + \dots \right]$$

$$= \varepsilon f(t) \left[c(0) + \varepsilon c_1(t) + \dots \right]$$

$\mathcal{O}(\varepsilon)$ terms: $\dfrac{d}{dt} c_1(t) = f(t) c(0)$

Simpler version: $\frac{dc}{dt} = \varepsilon \cdot f(t) \cdot c$

small

PERTURBATION THEORY: $c(t) = c(0) + \varepsilon c_1(t) + \varepsilon^2 c_2(t) + \ldots$

B) Solve this equation (given $c(0)$)

$$\frac{dc_1}{dt} = f(t)c(0)$$

$$c_1(t) = \int_0^t dt_1 f(t_1) c(0)$$

(want $c_1(0) = 0$)

Summary: For $\frac{dc}{dt} = \varepsilon f(t) \cdot c$

Perturbation theory gives $c(t) = c(0) + \varepsilon \int_0^t dt_1\, f(t_1)\, c(0) + O(\varepsilon^2)$

Exact: $\frac{dc}{dt} = \varepsilon f(t)\, c$

$$\Rightarrow \frac{1}{c}\frac{dc}{dt} = \varepsilon f(t)$$

$$\Rightarrow \frac{d}{dt}\big(\ln(c)\big) = \varepsilon f(t)$$

$$\Rightarrow \ln(c) = \varepsilon \int_0^t f(t_1)\, dt_1 + \text{const}$$

$$\Rightarrow c(t) = \text{const} \times e^{\varepsilon \int_0^t f(t_1)\, dt_1}$$

$$\Rightarrow c(t) = c(0) \times e^{\varepsilon \int_0^t f(t_1)\, dt_1}$$

$$\approx c(0) + \varepsilon \int_0^t dt_1\, f(t_1)\, c(0) + \cdots$$

Matches our perturbative result.

Summary: For $\frac{dc}{dt} = \varepsilon f(t) \cdot c$

Perturbation theory gives $c(t) = c(0) + \varepsilon \int_0^t dt_1\, f(t_1)\, c(0)$
$+ O(\varepsilon^2)$

Real equation:

$$\frac{dc_m}{dt} = -\frac{i}{\hbar} \sum_n e^{i(E_m - E_n)t/\hbar} H'_{mn}(t)\, c_n(t)$$

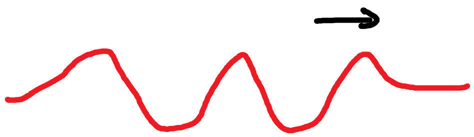
Same method gives

$$c_m(t) = c_m(0) - \frac{i}{\hbar} \sum_n \left[\int_0^t dt_1\, e^{i(E_m - E_n)t_1/\hbar} H'_{mn}(t_1) \right] c_n(0)$$
$$+ O(H'^2)$$

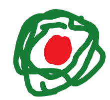
$$c_m(t) = c_m(0) - \frac{i}{\hbar}\sum_n \left[\int_0^t dt_1\, e^{i(E_m-E_n)t_1/\hbar}\, H'_{mn}(t_1)\right] c_n(0)$$

$$+\, O(H'^2)$$

EXAMPLE:



EM wave



ground state of hydrogen

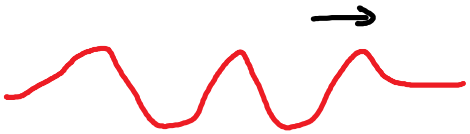
$$|\Psi(0)\rangle = |1\,0\,0\rangle$$

What is the probability that state will be $|n\,\ell\,m\rangle \neq |1\,0\,0\rangle$ after wave passes?

$$c_m(t) = c_m(0) - \frac{i}{\hbar}\sum_n \left[\int_0^t dt_1\, e^{i(E_m-E_n)t_1/\hbar}\, H'_{mn}(t_1)\right] c_n(0)$$

$$+\ O(H'^2)$$

EXAMPLE:



EM wave

ground state of hydrogen $\quad |\Psi(0)\rangle = |1\,0\,0\rangle$

What is the probability that state will be $|n\,l\,m\rangle \neq |1\,0\,0\rangle$ after wave passes? $\quad c_{100}(0) = 1 \quad$ all others 0

$$P_{nlm}(t) = |c_{nlm}(t)|^2 = \frac{1}{\hbar^2}\left|\int_0^t dt_1\, e^{-i(E_n-E_1)\frac{t}{\hbar}}\langle n\,l\,m|H'(t)|1\,0\,0\rangle\right|^2$$