

# Quantum mechanics

## Chapter VII Approximation Methods







- There are many complicated potentials for which Schrödinger's equation cannot be solved exactly. For such situations, we resort to approximation methods for finding approximate solutions to the Schrödinger equation.
- The perturbation theory is based on systematically obtaining an approximate solution to the perturbed system by developing solutions based on the exact solutions of the unperturbed case.
- To understand such approach, consider the following Hamiltonian:

$$H = H_0 + \lambda H_1$$



- where  $H_1$  is the perturbation,  $H_0$  is the Hamiltonian of the unperturbed system, and  $\lambda$  small number that varies between 0 and 1.
- The magnitude of this number decides how strong or how weak the perturbation is. For the unperturbed system

$$H_0 | \psi_n^{(0)} \rangle = E_n^{(0)} | \psi_n^{(0)} \rangle$$

- where the eigenvalues and eigenfunctions are already known or these can easily be obtained.
- Thus, the Schrödinger equation for the system now is:

$$(H_0 + \lambda H_1) | \psi_n \rangle = E_n | \psi_n \rangle$$

The eigenfunctions and eigenvalues of H must depend on  $\lambda$ , because H depends on  $\lambda$ . Therefore,  $\psi_n$  and  $E_n$  can be expanded in a power series with respect to  $\lambda$ , as follows:

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots$$

$$|\psi_n\rangle = |\psi_n^{(0)}\rangle + \lambda |\psi_n^{(1)}\rangle + \lambda^2 |\psi_n^{(2)}\rangle + \dots$$

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where we used the following abbreviations in the expansion:

$$E_n^{(k)} = \frac{1}{k!} \frac{\partial^k E_n}{\partial \lambda} \bigg|_{\lambda=0}$$
$$\psi_n^{(k)} = \frac{1}{k!} \frac{\partial^k |\psi_n\rangle}{\partial \lambda} \bigg|_{\lambda=0}$$

 $|\psi_n^{(n)}\rangle = \frac{1}{k!} \frac{1}{\partial \lambda}$ 

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The  $E_n$  and  $\psi_n$  of a system are the sum of the correction terms. It is obvious that the convergence of these power series is a key issue, because the series must be truncated in practice.

Therefore, we get

$$(H_0 + \lambda H_1) \left[ |\psi_n^{(0)}\rangle + \lambda |\psi_n^{(1)}\rangle + \lambda^2 |\psi_n^{(2)}\rangle + \dots \right] \\= \left[ E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots \right] \left[ |\psi_n^{(0)}\rangle + \lambda |\psi_n^{(1)}\rangle + \lambda^2 |\psi_n^{(2)}\rangle + \dots \right]$$

the simplification of which gives terms with various powers of  $\lambda$  on both the sides. This gives rise to:

$$H_0 | \psi_n^{(0)} \rangle = E_n^{(0)} | \psi_n^{(0)} \rangle$$



$$H_0 |\psi_n^{(1)}\rangle + H_1 |\psi_n^{(0)}\rangle = E_n^{(0)} |\psi_n^{(1)}\rangle + E_n^{(1)} |\psi_n^{(0)}\rangle$$

 $H_0 |\psi_n^{(2)}\rangle + H_1 |\psi_n^{(1)}\rangle = E_n^{(0)} |\psi_n^{(2)}\rangle + E_n^{(1)} |\psi_n^{(1)}\rangle + E_n^{(2)} |\psi_n^{(0)}\rangle$ 

They can be generalized to,

$$H_0 |\psi_n^{(k)}\rangle + H_1 |\psi_n^{(k-1)}\rangle = \sum_{i=0}^k E_n^{(i)} |\psi_n^{(k-i)}\rangle$$

We assume that eigenvectors of H are orthonormal, and hence  $\langle \psi^{(0)}m | \psi^{(0)}n \rangle = \delta_{mn}$ . The zeroth order energy is then obtained from:

$$E_n^{(0)} = \langle \psi_n^{(0)} | H_0 | \psi_n^{(0)} \rangle$$

## Time-independent perturbation



On operating with the wave function of unperturbed Hamiltonian from the left on both the sides of first-order equation E = E

We now consider the two possibilities: (i) m = n and (ii)  $m \neq n$  **n.** From the case of m = n, m = n E = H  $E_n^{(1)} = \langle \Psi_n^{(0)} | H_1 | \Psi_n^{(0)} \rangle$   $m \neq n$ 

and when  $m \neq n$  $m \neq n$ ,

 $m \neq n$ 

$$E_m^{(0)} \left\langle \boldsymbol{\psi}_m^{(0)} \middle| \boldsymbol{\psi}_n^{(1)} \right\rangle + \left\langle \boldsymbol{\psi}_m^{(0)} \middle| H_1 \middle| \boldsymbol{\psi}_n^{(0)} \right\rangle = E_n^{(0)} \left\langle \boldsymbol{\psi}_m^{(0)} \middle| \boldsymbol{\psi}_n^{(1)} \right\rangle$$
$$\Rightarrow \left\langle \boldsymbol{\psi}_m^{(0)} \middle| H_1 \middle| \boldsymbol{\psi}_n^{(0)} \right\rangle = \left( E_n^{(0)} - E_m^{(0)} \right) \left\langle \boldsymbol{\psi}_m^{(0)} \middle| \boldsymbol{\psi}_n^{(1)} \right\rangle$$

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### Therefore

$$\left(H_0-E_n^{(0)}\right)\left|\psi_n^{(1)}\right\rangle = \left(E_n^{(1)}-H_1\right)\left|\psi_n^{(0)}\right\rangle$$

which suggests that  $\psi^{(1)}$  can be constructed as a linear combination of exact solutions of H<sub>0</sub>, which provide a convenient but not a unique choice for a complete orthonormal basis.

The various order corrections  $\psi^{(k)}$  to the eigenstate can then also be constructed as a linear combination of exact solutions of H\_0,  $H_0$ 

$$\left| \boldsymbol{\psi}_{n}^{(k)} \right\rangle = \sum_{\mu} C_{n\mu}^{(k)} \left| \boldsymbol{\psi}_{\mu}^{(0)} \right\rangle$$

Time-intependent  $k_{k}$   $k_{m}$   $k_{$ 副大學 To find an expansion set ficient, we have not the for k=1  $(E_m^{(0)} - E_n^{(0)}) \sum C_{n\mu}^{(1)} \langle \psi_m^{(0)} | \psi_\mu^{(0)} \rangle = \langle \psi_m^{(0)} | H_1 | \psi_n^{(0)} \rangle$ which yields: $\Psi_m$  $\Psi_n$  $\begin{pmatrix} m & n \\ C_{nm}^{(1)} = \frac{\left\langle \boldsymbol{\Psi}_{m}^{(0)} \boldsymbol{\Psi}_{n}^{m} \middle| \boldsymbol{\Psi}_{n}^{(0)} \right\rangle^{n}}{\left( E_{\boldsymbol{W}_{m}}^{(0)} - E_{n}^{(0)} \right)^{n}} \end{pmatrix}$ 

This equation is  $\sqrt[n]{atial}$  only  $(f_{0,r}, m_{n} \neq n)$   $n_{r}^{m}$  if n is not matind for m = $m \neq n$ m = nn. We therefore obtain:

$$\begin{split} & \Psi^{(1)} & \Psi^{(1)} \\ \Psi^{(1)} & \left( \left| \Psi^{(1)}_{n} \right\rangle + A \left| \Psi^{(0)}_{n} \right\rangle \right)_{n}^{\left( n \right)} \\ \left( \left| \Psi^{(1)}_{n} \right\rangle + A \left| \Psi^{(0)}_{n} \right\rangle \right)_{n}^{\left( n \right)} \\ \Psi^{(1)} & \Psi^{(1)} \\ \Psi^{(1)} & \left( \left| \Psi^{(1)}_{n} \right\rangle + A \left| \Psi^{(0)}_{n} \right\rangle \right)_{n}^{\left( n \right)} \\ \Psi^{(1)} & \Psi^{(1)} \\ \Psi^{(1)} & \Psi^{$$

 $\Psi^{(1)}$ 02/12/2022

m = n

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n

### Time-independent perturbation

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also satisfies the Schrödinger equation of first-order wave function, for any constant A. This provides us freedom to subtract off the  $\psi^{(0)}$  for  $\pi$ , and therefore, there is no need to include the m = n term in the sum for constructing  $\psi^{(1)}$ 

To calculate  $\psi^{\mbox{the}}$  second-order corrections to energy, we have,

$$\left\langle \boldsymbol{\Psi}_{m}^{(0)} \middle| \boldsymbol{H}_{0} \middle| \boldsymbol{\Psi}_{n}^{(2)} \right\rangle + \left\langle \boldsymbol{\Psi}_{m}^{(0)} \middle| \boldsymbol{H}_{1} \middle| \boldsymbol{\Psi}_{n}^{(1)} \right\rangle =$$

$$E_{n}^{(0)} \left\langle \boldsymbol{\Psi}_{m}^{(0)} \middle| \boldsymbol{\Psi}_{n}^{(2)} \right\rangle + E_{n}^{(1)} \left\langle \boldsymbol{\Psi}_{m}^{(0)} \middle| \boldsymbol{\Psi}_{n}^{(1)} \right\rangle + E_{n}^{(2)} \left\langle \boldsymbol{\Psi}_{m}^{(0)} \middle| \boldsymbol{\Psi}_{n}^{(0)} \right\rangle$$

When we take m = n, the first term on the left-hand side cancels out the first term on the right-hand side,  $an_{\mu}d^{0}the = 0$ second term on the right-hand side vanishes.



 $\begin{array}{c} m \neq n \\ \hline \textbf{Jinniu Hu} & m \neq n \end{array}$ 



# Time-independent perturbation "

Therefore,  $\lambda \left( {}^{*}C_{nn}^{(1)} + (C_{nn}^{(1)})^{*} \right) + \lambda^{2} \left( {C_{nn}^{(2)} + (C_{nn}^{(2)})^{*} + \sum_{v} \left| C_{nv}^{(1)} \right|^{2}} \right) = 0$  周大學

 $C^{(1)} \subseteq (C^{(1)})^* = 0$ 

and

\*  $\sum_{\substack{n \in \mathbb{Z}^{n} \\ n \neq n}} C_{nn}^{(2)} + (C_{nn}^{(2)})^* = \sum_{\substack{n \in \mathbb{Z}^{n} \\ n \neq n}} |C_{nn}^{(1)}|^2$ The imaginary parts of the left-hand side of the last equation cancel out each other of the left-hand side of the last  $\operatorname{Re}(C_{nn}^{(2)}) = -\frac{1}{2} \sum_{\substack{n \in \mathbb{Z}^{n} \\ n \neq n}} |C_{nn}^{(1)}|^{\forall \neq n}$ 

 $C_{nn}^{(1)} + (C_{nn}^{(1)})^* = 0.$ 

We thus have,  $|\psi_{n}^{(2)}\rangle = \sum_{\nu \neq n} \sum_{\mu \neq n} \left[ \frac{\langle \Psi_{\mu}^{(0)} | H_{1} | \Psi_{n}^{(0)} \rangle \langle \Psi_{\nu}^{(0)} | H_{1} | \Psi_{\mu}^{(0)} \rangle}{(E_{\mu}^{(0)} - E_{\nu}^{(0)})} - \frac{\langle \Psi_{n}^{(0)} | H_{1} | \Psi_{n}^{(0)} \rangle \langle \Psi_{\mu}^{(0)} | H_{1} | \Psi_{n}^{(0)} \rangle}{(E_{\mu}^{(0)} - E_{\nu}^{(0)})} - \frac{\langle \Psi_{n}^{(0)} | H_{1} | \Psi_{n}^{(0)} \rangle}{(E_{\mu}^{(0)} - E_{n}^{(0)})^{2}} \right] |\Psi_{\mu}^{(0)}\rangle$   $- \frac{1}{2} \sum_{\nu \neq n} \frac{\left| \langle \Psi_{\nu}^{(0)} | H_{1} | \Psi_{n}^{(0)} \rangle \right|^{2}}{(E_{\nu}^{(0)} - E_{n}^{(0)})^{2}} |\Psi_{n}^{(0)}\rangle$ 

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As stated earlier, when there are more than one eigenvectors, the set of quantum numbers (nlm) takes more than one value, and all belong to same energy eigenvalue, the state is called the degenerate state.  $H_0$ 

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- When energy states of H<sub>0</sub> are degenerate, we can write  $H_0 |\psi_{n\alpha}^{(0)}\rangle = E_n^{(0)} |\psi_{n\alpha}^{(0)}\rangle$
- where  $\alpha$  takes values 1,2,3, ....r, for a given value of n. Thus,  $\alpha$ -labels<sup>n</sup> represents quantum numbers other than n in a complete set of (nlm). We say that the nth state is r-fold degenerate.  $H_0$

Time-independent perturb<sup> $\alpha$ </sup> ation  $n_{\alpha}$ 周大學 Within a degenerate subspace, any linear combination of wave function kets is another wave function ket<sup> $H_0$ </sup> f H<sub>0</sub>, with the same energy eigenvalue. Let us take the linear combination,  $\left|\phi_{n}^{(0)}\right\rangle = \sum_{r=0}^{r} D_{\alpha} \left|\psi_{n\alpha}^{(0)}\right\rangle.$ α •  $\alpha = 1$ 

which with the use of the above argument gives,

 $H_0\left|\phi_n^{(0)}\right\rangle = E_n^{(0)}\left|\phi_n^{(0)}\right\rangle$ 

We further say that the new set of wave function kets satisfies the orthonormality condition,

$$\left\langle \phi_{n\alpha}^{(0)} \middle| \phi_{n'\beta}^{(0)} \right\rangle = \delta_{nn'} \delta_{\alpha\beta} \text{ because } \left\langle \psi_{n\alpha}^{(0)} \middle| \psi_{n\beta}^{(0)} \right\rangle = \delta_{\alpha\beta}.$$

$$E \qquad E_n \qquad n$$
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$$E_n \qquad n$$





Its non-trivial solution demands:

$$\begin{array}{c|cccc} h_{11} - E_n^{(1)} & h_{12} & \cdots & h_{1r} \\ h_{21} & h_{22} - E_n^{(1)} & \cdots & h_{2r} \\ \vdots & \vdots & \vdots & \vdots \\ h_{r1} & h_{r2} & \cdots & h_{rr} - E_n^{(1)} \end{array} = 0$$

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周大學 **Time-independent perturbation** When all the r-values are non-zero and distinct, we have  $r_{E_n}$ nonzero nance distinct values of  $h_r$ h  $E_n = E_n^{(0)} + \lambda E_n^{(1)} \qquad ^n$  $E_{n}^{(1)}$ suggesting that the degeneracy is completely removed by  $\ddot{D}_{1}$ , perturbation. For the case when some of the r-values of  $E^{(1)}_n$  are zero or identical, degeneracy is partially removed. (1) (1) (1) (1) (1)  $n1 + n2 + n3 + \dots + n3$ The expansion coefficients  $D_1$ ,  $D_2$ ,  $D_3$ ....  $D_r$  are determined by solving above determinant along with the normalizing  $E_{n}^{(1)}$ condition of the wave function, which leads to  $D_1$ .

$$(l = 0, m = 0) \qquad D_1^{p_1} + D_2^2 + D_3^2 + \dots + D_r^2 = 1. (l = 1; m = 1, 0, -1)$$

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–*e* E.r



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### Linear Stark effect

The first excited state (n=2) of hydrogen is a four-fold degenerate state; there are one 2s-state ( $I = 0, \mathbb{R}^2 \pm \overline{0}^2$   $\pm \mathbb{R}^2 + \cdots$ three p-states (I = 1; m = 1,0,-1).

Let us suppose that the electric field E is applied along the pos(*itive*, *n*=-a0) is. The electric field 1; *interacts* 1; with the electron dipole moment. Since the field is along the z-axis, additional potential energy is (n=2)

$$H_1 = -e^{\left(\frac{l}{2} \cdot \frac{m}{e} - \frac{m}{e}\right)} \Phi r \cos \theta, \qquad \theta \qquad (l = 1; m = 1)$$

 $E_n = E_n^{(0)} + \lambda E_n^{(1)}$ 

 $-\rho' Fr cos$ 

 $\theta$  is an angle between the z-axis and r, and

$$e' = \frac{e}{\sqrt{4\pi\varepsilon_0}},$$

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Linear Stark effect 
$$e^{i} Er \cos \theta$$
  
 $B$   
 $E^{T}$   
In this case,  
 $|\psi_{21}^{(0)}\rangle = |\psi_{200}\rangle,$   
 $|\psi_{22}^{(0)}\rangle = |\psi_{210}\rangle,$   
 $- E \cos \theta$  '''  $|\psi_{23}^{(0)}\rangle = |\psi_{211}\rangle,$   
and  
 $- E \cos \theta$  '''  $|\psi_{24}^{(0)}\rangle = |\psi_{21-1}\rangle$   
and  
 $- E \cos \theta$  '''  $|\psi_{24}^{(0)}\rangle = |\psi_{21-1}\rangle$   
 $A \times 4$   
 $Wave functions for the hydrogen atom are
 $\int_{0}^{\pi} \int_{0}^{\pi} \psi_{nim}(r, \theta, \phi)(r \cos \theta)\psi_{n'l'm'}(r, \theta, \phi)r^{2}dr \sin \theta d\theta d\phi^{4} \times 4$   
Wave functions for the hydrogen atom are  
 $\int_{0}^{\pi} \psi_{200}(r) = \frac{1}{4a_{0}} (\frac{1}{2\pi a_{0}})^{1/2} (2 - \frac{q'}{a_{0}}) e^{-r/2a_{0}} \beta \theta \phi$   
 $\psi_{210}(r, \theta, \phi) = \frac{1}{4a_{0}} (\frac{1}{2\pi a_{0}})^{1/2} re^{-r/2a_{0}} \cos \theta, and$   
 $\psi_{21,41}(r, \theta, \phi) = \frac{1}{4a_{0}} (\frac{1}{\pi a_{0}^{3}})^{1/2} re^{-r/2a_{0}} (\sin \theta)e^{\pm i\phi}$$ 

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 $0; 211 H_1 210; 21, -1 H_1 21, 0 21, -1 211$  $\begin{array}{c} \textbf{Lin 200r}, \textbf{S10200} & \textbf{21021212} \\ \textbf{1} & 200; 21-1 \\ \textbf{200}; 21-1 \\ \textbf{200}; 21-1 \\ \textbf{200}; 211 \\ \textbf{H}_{1} \\ \textbf{210}; 21, -1 \\ \textbf{H}_{1} \\ \textbf{210}; 21, -1 \\ \textbf{H}_{1} \\ \textbf{210}; 21, -1 \\ \textbf{H}_{1} \\ \textbf{210} \\ \textbf{210}$ The remaining two non-zero matrix elements are 21,-1 21,-1 21,-1 $\langle 200|H_1|210\rangle$  and  $\langle 210|H_1|200\rangle$ q 0 200 210 210 200 and  $= -\frac{e'E}{24a_0^3} \int \frac{r}{a_0} \left(2 - \frac{r}{a_0}\right) r^2 e^{-r/a_0} dr$  $= -3e' Ea_0$ 

Since  $<200|H_1|210>$  is real, it is equal to  $<210|H_1|200>$ .

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The states |200> and |210> are affected on application of the electric field, while the states |211> and |21,-1> remain unaffected.

It can therefore be said that degeneracy has partially been 211 211 21,-1 lifted on the application field to the 2s and 2p states of the hydrogen atom. To evaluate eigenvectors, we solve:

$$\begin{bmatrix} -E_2^{(1)} & -3e'Ea_0 & 0 & 0 \\ -3e'Ea_0 & -E_2^{(1)} & 0 & 0 \\ 0 & 0 & -E_2^{(1)} & 0 \\ 0 & 0 & 0 & -E_2^{(1)} \end{bmatrix} \begin{bmatrix} D_1 \\ D_2 \\ D_3 \\ D_4 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \end{bmatrix}$$



### Linear Stark effect



The first excited state of the hydrogen atom in the presence of an electric field applied along the z-axis presents a permanent electric dipole moment of magnitude 3e'Ea, with three orientations: one state parallel to the electric field, one state antiparallel to the electric field, and two states with zero interaction with the electric field, in the first order linear Stark effect. Jinniu Hu 02/12/2022

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In solving the problems where it is hard to determine a good unperturbed Hamiltonian, to make the perturbation small and solvable, the variational method is more robust in comparison with the perturbation theory. The variational theorem states that the expectation value

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of the Hamiltonian <H> calculated with the use of a normalized trial wave function ket  $|\phi\rangle$  is always greater than or equal to  $E_g$ :  $E_g \leq \langle H \rangle = \langle \phi | H | \phi \rangle$ 

where

$$\langle \phi | \phi \rangle = 1.$$
  
 $\phi \phi = 1.$ 

Variation Method  

$$\psi_{\phi}$$
To prove when variational theorem, the  $\phi$  can formally be  
expanded as a linear combination of the exact wave  
function<sup>6</sup> kets  $\psi_{n}$  of the system.  
 $|\phi\rangle = \sum_{n} |\psi_{n}\rangle$ 
 $\sum_{n} n n$   
with  
 $U_{\eta_{n}} = E_{n} \psi$ 
 $\psi_{n} = E_{n} \psi$ 
 $\psi_{n} = E_{n} \psi$ 
 $\psi_{n} = \frac{1}{2} \sum_{n} e^{i(\psi_{n})} \sum_$ 

### Variation Method



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Any variations in the trial function which lower the computed energy necessarily bring the approximate energy closer to  $E_g$ .

An example soft the above laid down procedure is the calculation of the ground state energy of the hydrogen atom with the use of the variational method by taking the wave function

$$\phi(r) = A e^{-\alpha r}$$

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as a trial wave function, where  $\alpha$  is the variational parameter.

**育間大學** Variation Method  $= -\alpha r$ The ground state  $(\vec{l} = 0)$  Hamiltonian for the hydrogen 2 2 2 atom is given by:  $H = -\frac{\hbar^2}{2\mu} \left[ \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right] - \frac{\int e^2}{4\pi\varepsilon_0 r}$  $\phi(r)$ To find normalized  $\phi(\mathbf{r})$ , we take:  $1 = \langle \phi | \phi \rangle$  $=A^2 \int \int \int e^{-2\alpha r} r^2 dr \sin \theta d\theta d\phi$  $=4\pi A^2 \int_{0}^{\infty} e^{-2\alpha r} r^2 dr \quad \Theta$  $=4\pi A^2 \frac{2!}{(2\alpha)^3}$  $=A^2\frac{\pi}{\alpha^3}$  $\Rightarrow A = \frac{\alpha^{3/2}}{\sqrt{\pi}}$ 

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**Jinniu H4** $\pi\epsilon_0\hbar$ 

11 <sup>9</sup>the Ground State of the Helium Atom 副大 The helium atom consists of two helectrons revolving in an orbit around a nucleus having charge 2e. Taking the origin of the coordinate system at the nucleus and the two electrons at the distances of  $r_2(and)^2 n_2^2$  from the nucleus, as shown, Electron-1(-e)  $|\mathbf{r}_1 - \mathbf{r}_2|$ Electron-2(-e)



Nucleus (+ 2e)

Its Hamiltonian for the system is

$$H = -\frac{\hbar^2}{2\mu}\nabla_1^2 - \frac{2e^2}{4\pi\epsilon_0 r_1} - \frac{\hbar^2}{2\mu}\nabla_2^2 - \frac{2e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|}$$

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- We want to calculate the ground state energy for this system. Though it is a simple problem, it does not have an exact solution.
- We would like to compute the approximate ground state energy  $E_g$  that could be as close as possible with the experimentally measured value of -78.975 eV.
- If the electron-electron interaction,

$$V_{ee} = \frac{e^2}{4\pi\varepsilon_0 \left| \mathbf{r}_1 - \mathbf{r}_2 \right|}$$

is ignorable, then the Hamiltonian simply breaks into two hydrogen-like Hamiltonians, and the ground state energy  $e^2$  are

## The Ground State of the $\operatorname{Heli}_{\mathbf{r}}^{e^2}$ Atom

$$2\left\{-\frac{\mu(2e^2)^2}{2(4\pi\epsilon_0)^2\hbar^2} = -\frac{2e^2}{(4\pi\epsilon_0)a_0}\right\} = 8E_1 \left( \mu e^{2/2} e^2 \right)$$

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<sub>E1</sub>and the ground state wave function will be the product of two hydrogen-like wave functions:

$$\Psi(r) = \frac{8}{\pi a_0^3} e^{-2(r_1 + r_2)/a_0}$$

- We hence solve the problem with the use of the variational method to get  $E_g$ .
- On average, each electron represents a cloud of negative charge that partially screens the nucleus, so that another electron sees an effective charge on the nucleus, which 2eshould be somewhat less than 2e.

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This suggests that a more realistic trial wave function cap be taken as,  $^{2e}$ 

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$$\phi(r) = \frac{Z^{3}}{\pi a_{0}^{3}} e^{-Z(r_{1}+r_{2})/a_{0}} = \frac{1}{\sqrt{\pi}} \left( \frac{Z}{a_{0}^{3}} \right)^{3/2}_{-a_{0}} e^{-Zr_{1}/a_{0}} \times \frac{1}{\sqrt{\pi}} \left( \frac{Z}{a_{0}} \right)^{3/2}_{-a_{0}} e^{-Zr_{2}/a_{0}} = \phi_{1}(r_{1})\phi_{2}(r_{2})$$
where Z is the variational parameter to be determined.  
The Hamiltonian Zef helium can be rewritten as  $(Z-2)e^{2}$ ,  $(Z-2)e^{2}$   
 $H = -\frac{\hbar^{2}}{2\mu} \nabla_{1}^{2} - \frac{Ze^{2}}{4\pi\epsilon_{0}r_{1}} - \frac{\hbar^{2}}{2\mu} \nabla_{2}^{2} - \frac{Ze^{2}}{4\pi\epsilon_{0}r_{2}} + \frac{e^{2}}{4\pi\epsilon_{0}r_{2}} + \frac{(Z-2)e^{2}}{4\pi\epsilon_{0}r_{1}} + \frac{(Z-2)e^{2}}{4\pi\epsilon_{0}r_{1}} + \frac{(Z-2)e^{2}}{4\pi\epsilon_{0}r_{2}}$ 

The expectation value of the Hamiltonian is

$$\langle H \rangle = 2Z^2 E_1 + (Z-2) \frac{e^2}{4\pi\epsilon_0} \left\langle \frac{1}{r_1} \right\rangle + (Z-2) \frac{e^2}{4\pi\epsilon_0} \left\langle \frac{1}{r_2} \right\rangle + \frac{e^2}{4\pi\epsilon_0} \left\langle \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right\rangle$$



#### where

$$\left\langle \frac{1}{r_1} \right\rangle = \left\langle \phi \right| \frac{1}{r_1} \left| \phi \right\rangle$$
$$= \frac{Z^3}{\pi a_0^3} \int_{0}^{\infty} \int_{0}^{\pi 2\pi} e^{-2Zr_1/a_0} r_1 dr_1 \sin \theta d\theta d\phi$$
$$= \frac{4Z^3}{a_0^3} \int_{0}^{\infty} e^{-2Zr_1/a_0} r_1 dr_1$$
$$= \frac{4Z^3}{a_0^3} \frac{a_0^2}{4Z^2}$$
$$= \frac{Z}{a_0}$$
$$_2 \quad \left\langle \frac{1}{r_2^0} \right\rangle = \frac{Z}{a_0}.$$

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and
We next evaluate:

$$\left\langle \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right\rangle^2 = \left( \frac{Z^3}{\pi a_0^3} \right)^2 \int \frac{e^{-2Z(r_1 + r_2)/a_0}}{|\mathbf{r}_1 - \mathbf{r}_2|} \frac{d^3r_1 d^3r_2}{dr_1} dr_2$$

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To evaluate this integral, we first fix  $r_1$  alone the  $z_2$  axis and then choose the coordinate system for  $r_2$ 







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### which yields,

$$I = 4\pi \left[ \int_{0}^{r_{1}} \frac{e^{-2Zr_{2}/a_{0}}}{r_{1}} r_{2}^{2} dr_{2} + \int_{r_{1}}^{\infty} \frac{e^{-2Zr_{2}/a_{0}}}{r_{2}} r_{2}^{2} dr \right]$$
$$= \frac{\pi a_{0}^{3}}{Z^{3}r_{1}} \left[ 1 - \left( 1 + \frac{Zr_{1}}{a_{0}} \right) e^{-2Zr_{1}/a_{0}} \right]$$

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### Therefore,

$$\left\langle \frac{1}{|\mathbf{r}_{1} - \mathbf{r}_{2}|} \right\rangle = \frac{Z_{\pi}^{3}}{\pi a_{0}^{3}} \int_{0}^{\infty} \int_{0}^{\pi} \int_{0}^{\pi} \int_{0}^{2\pi} \left[ 1 - \left( 1 + \frac{Zr_{1}}{a_{0}} \right) e^{-2Zr_{1}/a_{0}} \right] e^{-2Zr_{1}/a_{0}} r_{1} dr_{1} \sin \theta_{1} d\theta_{1} d\phi_{1}$$

$$= \frac{4Z^{3}}{a_{0}^{3}} \int_{0}^{\infty} \left[ 1 - \left( 1 + \frac{Zr_{1}}{a_{0}} \right) e^{-2Zr_{1}/a_{0}} \right] e^{-2Zr_{1}/a_{0}} r_{1} dr_{1}$$

$$= \left( \frac{4Z^{3}}{a_{0}^{3}} \right) \left[ \int_{0}^{\infty} e^{-2Zr_{1}/a_{0}} r_{1} dr_{1} - \int_{0}^{\infty} e^{-4Zr_{1}/a_{0}} r_{1} dr_{1} - \frac{Z}{a_{0}} \int_{0}^{\infty} e^{-4Zr_{1}/a_{0}} r_{1}^{2} dr_{1} \right]$$

$$= \left( \frac{4Z^{3}}{a_{0}^{3}} \right) \left[ \frac{a_{0}^{2}}{4Z^{2}} - \frac{a_{0}^{2}}{16Z^{2}} - \frac{a_{0}^{2}}{32Z^{2}} \right] = \frac{5Z}{8a_{0}}$$

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Finally,

$$\langle H \rangle = 2Z^{2}E_{1} + (Z-2)\frac{e^{2}}{4\pi\varepsilon_{0}}\frac{Z}{a_{0}} + (Z-2)\frac{e^{2}}{4\pi\varepsilon_{0}}\frac{Z}{a_{0}} + \frac{e^{2}}{4\pi\varepsilon_{0}}\frac{5Z}{8a_{0}}$$

$$= 2Z^{2}E_{1} + \frac{e^{2}}{4\pi\varepsilon_{0}}\left(2Z-4+\frac{5}{8}\right)\frac{Z}{a_{0}}$$

$$= 2Z^{2}E_{1} - \left(4Z^{2}-\frac{27}{4}Z\right)E_{1}$$

$$= \left(-2Z^{2}+\frac{27}{4}Z\right)E_{1}$$

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Application of the variational method requires that <H> be minimized with respect to Z,

$$\frac{\partial \langle H \rangle}{\partial Z} = 0$$

$$\Rightarrow \left( -4 \mathbb{Z} + \frac{27}{4} \right) \mathbb{E} = 0$$

$$\Rightarrow Z_{\min} = \frac{27}{16} = 1.69$$

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The Ground State of the Helium Atom

which tells that the other electron screens the nucleus and reduces its charge from 2e to 1.69e. Thus, the grounddestate energy for helium is

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$$E_g = \left(-2(1.69)^2 + \frac{27}{4} \times 1.69\right) E_1$$
  
= 5.696 × E<sub>1</sub>  
= -77.46 eV

which is a reasonable result when compared with the experimental value -78.975 eV. The ground state energy of helium had been calculated with the use of a more  $_{E}e_{=-78.7}$  complicated trial wave function having a larger number of adjustable parameters and  $E_{g} = -78.7$  eV was achieved.

- 周大學 A more convenient method would be to write the trial wave function ket as a linear combination of known fixed basis vectors and then treat the expansion coefficients  $\underline{a}_{787}^{E}$
- a variational parameter.
- Let us assume that the basis vectors from a complete set and the trial wave function ket is

$$\sum_{i=1}^{k} \sum_{i=1}^{k} c_i |\psi_i\rangle, \text{ where } c_i (i = 1, 2, 3, ....)$$

are real or complex variational parameters. We then have,

$$\langle \phi | \phi \rangle = \sum_{i} c_{i}^{*} \langle \psi_{i} | \sum_{j} c_{j} | \psi_{j} \rangle = \sum_{i} \sum_{j} c_{i}^{*} \langle \psi_{i} | \psi_{j} \rangle^{i} \qquad j$$

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### and

$$\langle \phi | H | \phi \rangle = \left( \sum_{i}^{*} c_{i}^{*} \langle \psi_{i} | \right) H \left( \sum_{j} c_{j} | \psi_{j} \rangle \right) = \sum_{i} \sum_{j} c_{i}^{*} c_{i} \langle \psi_{i} | H | \psi_{j} \rangle$$

This gives

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### where we defined

$$h_{ij} = \langle \Psi_i | H | \Psi_j \rangle$$
 and  $s_{ij} = \langle \Psi_i | \Psi_j \rangle$ .

To find ground state energy, we minimize k = 1, 2Ho the variational parameter  $c_{i}^{*}$ 

$$c_k^* \quad \frac{\partial \langle H \rangle}{\partial c_k^*} = 0$$
, where  $k = 1, 2, 3....$  \*  $k = 1, 2, 3....$ 

We have

$$\frac{\partial}{\partial c_k^*} \left[ \langle H \rangle \sum_i \sum_j c_i^* c_j s_{ij} - \sum_i \sum_{j \neq i} c_i^* c_j h_{ij} \right]$$

$$= \frac{\partial \langle H \rangle}{\partial c_k^*} \sum_i \sum_j c_i^* c_j s_{ij} + \langle H \rangle \sum_j c_j s_{kj} - \sum_j c_j h_{kj}$$

$$\Rightarrow \frac{\partial \langle H \rangle}{\partial c_k^*} = \frac{\sum_j c_j h_{kj} - \langle H \rangle \sum_j c_j s_{kj}}{\sum_j \sum_i c_i^* c_j s_{ij}}$$



### Therefore

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$$\sum_{i} c_{j} h_{kj} - \langle H \rangle \sum_{i} c_{j} s_{kj} = \sum_{i} \begin{pmatrix} h_{kj} - \langle H \rangle s_{kj} \\ - \end{pmatrix} \begin{pmatrix} c_{j} = 0 \\ - \end{pmatrix} = 0,$$

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### and its expansion form is

$$\begin{bmatrix} h_{11} - \langle H \rangle s_{11} & h_{12} - \langle H \rangle s_{12} & \dots & h_{1n} - \langle H \rangle s_{1n} \\ h_{21} - \langle H \rangle s_{21} & h_{22} - \langle H \rangle s_{22} & \dots & h_{2n} - \langle H \rangle s_{2n} \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ h_{n1} - \langle H \rangle s_{n1} & h_{n2} - \langle H \rangle s_{n2} & \dots & h_{nn} - \langle H \rangle s_{nn} \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ \vdots \\ 0 \end{bmatrix}$$

### the non-trivial solution of which demands:

$$\begin{array}{c|ccccc} h_{11} - \langle H \rangle s_{11} & h_{12} - \langle H \rangle s_{12} & \dots & h_{1n} - \langle H \rangle s_{1n} \\ h_{21} - \langle H \rangle s_{21} & h_{22} - \langle H \rangle s_{22} & \dots & h_{2n} - \langle H \rangle s_{2n} \\ \vdots & \vdots & \vdots & \vdots \\ h_{n1} - \langle H \rangle s_{n1} & h_{n2} - \langle H \rangle s_{n2} & \dots & h_{nn} - \langle H \rangle s_{nn} \end{array} = 0$$

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### Variational Method for Excited States

If we denote the wave function=ket of  $\psi$  the ground state of a system by  $\phi_0$  then the energy of the first  $\phi$  excited state can be given by

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$$E_{1} = \langle \phi_{1} | H | \phi_{1} \rangle_{\min}$$

$$E = \phi \quad H \phi$$

$$\lim_{\infty} \psi = \psi \quad H \phi \quad \min_{\infty} \psi = \psi \quad H \phi$$

$$\lim_{\alpha \to \infty} \psi = \psi \quad H \phi \quad \min_{\alpha \to \infty} \psi = \psi \quad H \phi$$

$$\lim_{\alpha \to \infty} \psi = \psi \quad H \phi \quad \min_{\alpha \to \infty} \psi = \psi \quad H \phi \quad \min_{\alpha \to \infty} \psi = \psi \quad H \phi$$

<sup> $\infty$ </sup>In a similar manner, the energy of the second excited <sub>n=</sub>state will be given by

$$E_{2} = \langle \phi_{2} | H_{E} | \phi_{2} \rangle_{\text{min}} H \phi_{\text{min}}$$
under the condition
$$\phi \phi = 1_{\langle \phi_{2} | \phi_{2} \rangle} \phi = 1 \text{ and } \langle \phi_{2} | \phi_{1} \rangle = 0 = \langle \phi_{2} | \phi_{0} \rangle.$$

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### Variational Method for Excited States



### The Hamiltonian of a 1D harmonic oscillator is:

 $\frac{\hbar^{2}}{2m}\frac{d^{2}}{dx} = -\frac{\hbar^{2}}{2m}\frac{mt\partial^{2}x^{2}1}{dx^{2}} + \frac{1}{2}m\omega^{2}x^{2}$ Its ground state wave can  $\hbar^{2}ed^{2}written as_{2}$   $\frac{\hbar^{2}}{2m}\frac{d^{2}x^{2}}{dx^{2}} = 2$   $\frac{\hbar^{2}}{$ 

since



 $\infty$ 

 $-\infty$ 

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### Variational Method for Excited States

The normalization condition then gives:

$$I = B^{2} \int_{-\infty}^{\infty} x^{2} e^{-2\beta x^{2}} dx$$
$$= 2B^{2} \int_{0}^{\infty} x^{2} e^{-2\beta x^{2}} dx$$
$$= 2B^{2} \frac{\sqrt{\pi}}{4} \frac{1}{(2\beta)^{3/2}}$$
$$\Rightarrow B = 2\left(\frac{2}{\pi}\right)^{1/4} \beta^{3/4}$$

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### Next, we evaluate

 $\phi_1 H \phi_1$   $H\phi_1 = B \left[ -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} m \omega^2 x^2 \right] x e^{-\beta x^2}$   $= \hbar B \left[ \frac{3\hbar^2 \beta}{m} x + \left( \frac{1}{2} m \omega^2 - \frac{2\hbar^2 \beta^2}{m} \right) x^3 \right] e^{-\beta x^2}$ 



Variational Method for Excited States (



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On evaluating integrals and the substituting the value of  $B^2$  we get  $3\hbar^2\beta - 3m\omega^2$ 

Therefore  $\phi_1 \phi_1 \phi_1 \phi_1 \phi_1 \phi_1 \phi_1 \phi_1$ and

$$\begin{array}{ccc} \beta_{\phi_1} & \beta \beta & = \frac{m\omega}{\beta_2 n} \beta = \frac{m\omega}{\beta 2 \hbar} & \beta & = \frac{m\omega}{\beta 2 \hbar} \\ \beta & \beta & = \frac{m\omega}{2 \hbar} \end{array}$$

$$E_{1} = \left\langle \phi_{1} \right| \mathcal{H} \left| \phi_{1} \right\rangle_{\min} \mathcal{H} = \frac{3}{2} \mathcal{H}_{\omega} \frac{3}{2} \mathcal{H}_{H} \qquad \phi_{1} \frac{3}{2} \frac{2}{2} \left( \frac{2}{\pi} \right)^{1/4} \left( \frac{m\omega}{2\hbar} \right)^{3/4} x e^{-\beta x^{2}}$$

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The Hamiltonian for an N-electron system such as a metal or a large atom is

 $\sum_{i=1}^{N} \left( -\frac{\hbar^{2}}{2m} \nabla_{i}^{2} + V_{ext}(r_{i}) + \frac{1}{2} \sum_{j \neq i} \frac{e^{2}}{4\pi\epsilon_{0} |\mathbf{r}_{i} - \mathbf{r}_{j}|} \right)$ where single electron potential at the position  $\mathbf{r}_{i}$  is  $\mathbf{r}_{i} \quad V_{ext}(r_{i}) = -\frac{Ze^{2}}{4\pi\epsilon_{0}} \sum_{R}^{\mathbf{r}} \frac{1}{|\mathbf{r}_{i} - \mathbf{R}|}^{R} \quad \sum_{R}^{R} \mathbf{r} \quad \mathbf{R}$ 2 with R a position vector of a bare nuclei. The N-electrons wave function  $\psi(\mathbf{r}_1\mathbf{s}_1,\mathbf{r}_2\mathbf{s}_2,\mathbf{r}_3\mathbf{s}_3,\dots,\mathbf{r}_N\mathbf{s}_N)$ ,  $\mathbf{r}_1\mathbf{s}_1 \equiv \mathbf{i}$  representing both position and spin coordinates, satisfies the  $\Psi(\mathbf{r} s, \mathbf{r} s,$ Schrödinger equation:

$$H\psi = E\psi$$

### Systems of N-Electrons



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- The exact solution of this equation is not possible, and hence one looks for an approximate solution that ris, most s,..... reasonable. An electron interacts with N-1 electrons, in addition to its interaction which Fuelei.
- The methods based on the variational principle have been found most successful and reasonable approximations to solve the N-electrons Schrödinger equation. The variational principle assumes that the equation,

$$\frac{\delta}{\delta|\psi\rangle} \Big\{ \langle \psi|H|\psi\rangle - E \langle \psi|\psi\rangle \Big\} = 0$$

is equivalent to the Schrödinger equation.

Systems of N-Electrons 
$$d^{3}r$$
  
More explicitly, if we take the functional derivative of  
 $\psi^{*}()$   
 $(H-E) = \int \psi^{*}_{+} H^{\psi}(\mathbf{r}) - E\psi(\mathbf{r}) = \int \psi^{*}_{+} (\mathbf{r}) H^{\psi}(\mathbf{r}) d^{3}r$   
with respect to  $\psi^{*}(\mathbf{r})$ , we get  $\delta\psi^{*}()$   
 $H^{\psi}(\mathbf{r}) - E\psi(\mathbf{r}) = 0$   
 $\psi^{*}()$   
 $H^{\psi}(\mathbf{r}) - E\psi(\mathbf{r}) = 0$   
 $\psi^{*}()$   
 $H^{\psi}(\mathbf{r}) = E^{\psi}(\mathbf{r}) = \int (f^{*}_{+} \psi(\mathbf{r}) - E\psi(\mathbf{r})] \delta\psi^{*}(\mathbf{r}) d^{3}r$   
We can rewrite the Hamiltonian of multi-fectrons  $as_{\psi^{*}()}$   
follows,  $H^{\psi}(\mathbf{r}) \in \psi(\mathbf{r}) \in 0$   
 $\sum_{k} \sum_{k} H_{k} = \sum_{k}^{N} (H_{k} + \frac{1}{2} \sum_{k} V_{k}) \hbar^{2}$ 

 $\sum_{i=1}^{\infty} H = \sum_{i=1}^{\infty} \left( H_i + \frac{1}{2} \sum_{j \neq i}^{\infty} V_{ij} \right) \frac{h^2}{2m} \quad i \quad t(i)$ 

$$H_{i} = -\frac{\hbar^{2}}{2m}\nabla_{i}^{2} + V_{ext}(\mathbf{r}_{i})\sum_{j=1}^{2} h_{j}^{2} \qquad \sum_{j=1}^{i} \frac{e^{2}}{4\pi\varepsilon_{0}|\mathbf{r}_{i} - \mathbf{r}_{j}|}$$

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with

Hartree Approximation

 $=\delta_{ij}$ 

### We take the trial wave function as

$$\psi(1,2,3,...,N) = \phi_1(1_1)\phi_2(2)\phi_3(3)...,\phi_N(N)$$

 $e^{2}$ 

 $\mathbf{r}_i \quad \mathbf{r}_j$ 

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with

$$\langle \phi_i(\mathbf{r}_i s_i) | \phi_j(\mathbf{r}_j s_j) \rangle = \delta_{ij}$$

We have

$$\langle \boldsymbol{\psi} | \boldsymbol{H} | \boldsymbol{\psi} \rangle$$

$$= \sum_{i=1}^{N} \int d^{3}r_{1} \int d^{3}r_{2} \dots \int d^{3}r_{i} \dots \int d^{3}\overline{r_{N}} \phi_{1}^{*}(\mathbf{r}_{1}) \phi_{2}^{*}(\mathbf{r}_{2}) \dots \phi_{i}^{*}(\mathbf{r}_{i}) \dots \phi_{N}^{*}(\mathbf{r}_{N})$$

$$\times \left\{ H_{i} + \sum_{j \neq i} V_{ij} \right\} \phi_{1}(\mathbf{r}_{1}) \phi_{2}(\mathbf{r}_{2}) \dots \phi_{i}(\mathbf{r}_{i}) \dots \phi_{N}(\mathbf{r}_{N})$$

## Hartree Approximation

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## Here, $\int d^3r_1 \int d^3r_2 \dots \int d^3r_i \dots \int d^3r_N \phi_1^*(\mathbf{r}_1) \phi_2^*(\mathbf{r}_2) \dots \phi_i^*(\mathbf{r}_i) \dots \phi_N^*(\mathbf{r}_N) H_i \phi_1(\mathbf{r}_1) \phi_2(\mathbf{r}_2) \dots \phi_i(\mathbf{r}_i) \dots \phi_N(\mathbf{r}_N)$ $= \int d^3 r_i \phi_i^*(\mathbf{r}_i) H_i \phi_i(\mathbf{r}_i)$

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 $(\mathbf{r}_N)$ 

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Note that because  $H_i$  operates only  $O_{i}(r_i)$  and *i*fitegration over each of the other coordinates is equal to one. The electron-electron interaction term simplifies to  $\phi_i(\mathbf{r}_i)$  $H_i$  $\int \int d^3 r_i d^3 r_i \phi_i^*(\mathbf{r}_i) \phi_i(\mathbf{r}_i) V_{ii} \phi_i(\mathbf{r}_i) \phi_i(\mathbf{r}_i).$  $\mathbf{r}_{j}(\mathbf{r}_{j})$ 

and

$$\langle \Psi | H | \Psi \rangle \stackrel{H}{=} \sum_{i=1}^{N} \int d^{3}r_{i} \phi_{i}^{*}(\mathbf{r}_{i}) \left\{ H_{i} \phi_{i}(\mathbf{r}_{i}) + \frac{1}{2} \sum_{j(\neq i)=1}^{N} \int d^{3}r_{j} \phi_{j}^{*}(\mathbf{r}_{j}) V_{ij} \phi_{j}(\mathbf{r}_{j}) \phi_{i}(\mathbf{r}_{i}) \right\} \phi_{k}^{*}(\mathbf{r}_{k})$$

$$\underbrace{\Psi H \Psi}_{\text{Jinniu Hu}} \Phi_{k}^{*}(\mathbf{r}_{k})$$

To minimize  $\langle \psi | H | \psi \rangle$ , we take the functional derivative with respect to  $\phi^*_k(\mathbf{r}_k)$  and obtain,  $\phi_k^*(\mathbf{r}_k)$  $\int d^3 r_k \delta \phi_k^*(\mathbf{r}_k) \left\{ H_k \phi_k(\mathbf{r}_k) + \sum_{j(\neq k)=1}^N \int d^3 r_j \phi_j^*(\mathbf{r}_j) V_{kj} \phi_j(\mathbf{r}_j) \phi_k(\mathbf{r}_k) \right\} = 0$ It is to be noted that the factor of 1/2 before interaction term drops out because two equal terms, one for i = kand the other for j = k k appear when we take the ) derivative with respect to  $\phi^*_k$  (  $r_k$  ).

Due to the normalization of wave function, we have  

$$\varepsilon_k \int d^3 r_k \delta \phi_k^*(\mathbf{r}_k) \phi_k(\mathbf{r}_k) = 0$$
 with  $k = 1, 2, 3, ....N$ 

k

# Hartree Approximation

k



Here,  $\varepsilon_k$  is a multiplying constant. Finally, we have

$$\int d^3 r_k \, \delta \phi_k^*(\mathbf{r}_k) \left\{ H_k \phi_k(\mathbf{r}_k) + \sum_{j(\neq k)=1}^N \int d^3 r_j \phi_j^*(\mathbf{r}_j) V_{kj} \phi_j(\mathbf{r}_j) \phi_k(\mathbf{r}_k) - \varepsilon_k \phi_k(\mathbf{r}_k) \right\} = 0$$

Do make it stationary, the variations are zero for  $\delta \Phi^*(\mathbf{r}_k)$  possible forms of  $\delta \phi^*(\mathbf{r}_k)$ ; hence we can get

$$H_k \Phi_k(\mathbf{r}_k) + \sum_{j(\neq k)=1}^N \int d^3 r_j \Phi_j^*(\mathbf{r}_j) V_{kj} \Phi_j(\mathbf{r}_j) \Phi_k(\mathbf{r}_k) = \varepsilon_k \Phi_k(\mathbf{r}_k)^*$$

More explicitly,

$$\left\{-\frac{\hbar^2}{2m}\nabla_i^2 + V_{ext}(\mathbf{r}_i) + \frac{e^2}{4\pi\varepsilon_0}\sum_{j(\neq i)=1}^N \int d^3r_j \phi_j^*(\mathbf{r}_j) \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \phi_j(\mathbf{r}_j)\right\} \phi_i(\mathbf{r}_i) = \varepsilon_i \phi_i(\mathbf{r}_i)$$

which is an integro-differential equation, commonly known as the Hartree equation.  $r_i$ 

In 1927, D. R. Hartree introduced a procedure, which he called the self-consistent field method, to calculate approximate wave functions and energies for atoms and ions. His first proposed method of solution became known as the Hartree method, or Hartree product.



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### Mean-Field approximation







V

It is an eigenvalue equation for an electron located at position  $\mathbf{r}_i$  and moving under the influence of an effective potential,  $V(\mathbf{r}) = V(\mathbf{r}) + V(\mathbf{r})$  $V_{eff}(\mathbf{r}_i) = V_{ext}(\mathbf{r}_i) + V_{ee}(\mathbf{r}_i)$ 

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and

$$V_{ee}(\mathbf{r}_i) = \frac{e^2}{4\pi\varepsilon_0} \sum_{j\neq i} \int d^3 r_j \frac{\left|\phi_j(\mathbf{r}_j)\right|^2}{\left|\mathbf{r}_i - \mathbf{r}_j\right|}$$

The simple interpretation of this is as follows. The ith electron interacts with both nuclei and the remaining N-1 electrons. We thus find that the Hartree approximation onverts the N-particle problem into a set of N-single particle equations that that the problem  $\sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{i=1}^{n} \sum_{$ 

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In the Hartree approximation, the exchange effect is not taken care, which demands that the wave function for a system of N-Fermions  $m_N s_N^*$  be anti-symmetric,

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$$\psi_{a}(\mathbf{r}_{1},\mathbf{r}_{2},\ldots,\mathbf{r}_{N}) \stackrel{\mathbf{r}}{=} \frac{1}{\sqrt{N!}} \sum_{n_{1}=1}^{N} \sum_{n_{2}=1}^{N} \cdots \sum_{n_{N}=1}^{N} \sum_{n_{N}=1}^{N} \sum_{n_{1}=1}^{N} \sum_{n_{N}=1}^{N} \sum_{n_{N}=1}^{N}$$

Let us first evaluate the matrix element of  $H_i$ 

$$\left\langle \Psi_{a} \left| H_{i} \right| \Psi_{a} \right\rangle$$

$$= \frac{1}{N!} \int d^{3}r_{1} d^{3}r_{2} \dots d^{3}r_{N} \left[ \sum_{n_{1}=1}^{N} \sum_{n_{2}'=1}^{N} \dots \sum_{n_{N}'=1}^{N} \sum_{n_{1}'=1}^{N} \sum_$$

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There will be an integral over  $(N!)^2$  terms, where each term involves a product of the N wave!) functions and an equal number of their  $\frac{N}{c}$  of mplex conjugates. To understand the simplification of this equation, let us consider a case<sub>r</sub>, r of two electrons situated at  $r_i$  and  $r_j$ .

 $N \left\{ N \right\}$ 

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 $\langle \Psi_a | H_i | \Psi_a \rangle$ 

$$=\frac{1}{2!}\int d^{3}r_{i}d^{3}r_{j}\left[\sum_{n_{1}^{\prime}=1}^{2}\sum_{n_{2}^{\prime}=1}^{2}\in_{n_{1}n_{2}^{\prime}}\left\{\phi_{n_{1}^{\prime}}(\mathbf{r}_{i})\phi_{n_{2}^{\prime}}(\mathbf{r}_{j})\right\}^{*}\right]H_{i}\left[\sum_{n_{1}=1}^{2}\sum_{n_{2}=1}^{2}\in_{n_{1}n_{2}}\mathbf{r}_{i}\mathbf{r}_{i}\mathbf{r}_{i}\phi_{n_{1}}(\mathbf{r}_{i})\phi_{n_{2}}(\mathbf{r}_{j})\right]$$

Using  $\in = 0$   $\in_{12} = - \in_{12} = 0$  and  $e_{12} = - e_{21} = 1,$ the equation reduces to

$$\langle \Psi_a | H_i | \Psi_a \rangle$$
  
=  $\frac{1}{2!} \int d^3 r_i d^3 r_j \Big[ \phi_1^*(\mathbf{r}_i) \phi_2^*(\mathbf{r}_j) - \phi_2^*(\mathbf{r}_i) \phi_1^*(\mathbf{r}_j) \Big] H_i \Big[ \phi_1(\mathbf{r}_i) \phi_2(\mathbf{r}_j) - \phi_2(\mathbf{r}_i) \phi_1(\mathbf{r}_j) \Big]$ 

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### which expands to

$$\langle \boldsymbol{\psi}_{a} | H_{i} | \boldsymbol{\psi}_{a} \rangle$$

$$= \frac{1}{2!} \left[ \int d^{3}r_{i} \int d^{3}r_{j} | \boldsymbol{\phi}_{2}(\mathbf{r}_{j}) |^{2} \boldsymbol{\phi}_{1}^{*}(\mathbf{r}_{i}) H_{i} \boldsymbol{\phi}_{1}(\mathbf{r}_{i}) + \int d^{3}r_{i} \int d^{3}r_{j} | \boldsymbol{\phi}_{1}(\mathbf{r}_{j}) |^{2} \boldsymbol{\phi}_{2}^{*}(\mathbf{r}_{i}) H_{i} \boldsymbol{\phi}_{2}(\mathbf{r}_{i}) \right]$$

$$- \frac{1}{2!} \left[ \int d^{3}r_{i} \left\{ \int d^{3}r_{j} \boldsymbol{\phi}_{2}^{*}(\mathbf{r}_{j}) \boldsymbol{\phi}_{1}(\mathbf{r}_{j}) \right\} \boldsymbol{\phi}_{1}^{*}(\mathbf{r}_{i}) H_{i} \boldsymbol{\phi}_{2}(\mathbf{r}_{i}) + \int d^{3}r_{i} \left\{ \int d^{3}r_{j} \boldsymbol{\phi}_{1}^{*}(\mathbf{r}_{j}) \boldsymbol{\phi}_{2}(\mathbf{r}_{j}) \right\} \boldsymbol{\phi}_{2}^{*}(\mathbf{r}_{i}) H_{i} \boldsymbol{\phi}_{2}(\mathbf{r}_{i}) + \int d^{3}r_{i} \left\{ \int d^{3}r_{j} \boldsymbol{\phi}_{1}^{*}(\mathbf{r}_{j}) \boldsymbol{\phi}_{2}(\mathbf{r}_{j}) \right\} \boldsymbol{\phi}_{2}^{*}(\mathbf{r}_{i}) H_{i} \boldsymbol{\phi}_{1}(\mathbf{r}_{i}) \right] \mathbf{r}$$

The second term becomes identical to the first term on rinterchanging integrals over  $r_i$  and  $r_j$ .

$$\langle \Psi_a | H_i | \Psi_a \rangle = \int d^3 r_i \phi_1^*(\mathbf{r}_i) H_i \phi_1(\mathbf{r}_i)$$

However, in place of suffix 1, we can  $\forall s e^{H} d^{V}$  more generalized suffix n to write:  $\psi H \psi$ 

$$\langle \Psi_a | H_i | \Psi_a \rangle = \int d^{\mathcal{B}_i} r_i \phi^*_{n_i}(\mathbf{r}_i) H_i \phi_{n_i}(\mathbf{r}_i)$$

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#### Hartree-Fock Approximation $j \Psi_a$ $\Psi_j \Psi_a$



We find that for a two-electrons system,

$$\langle \boldsymbol{\psi}_{a} | \boldsymbol{V}_{ij} | \boldsymbol{\psi}_{a} \rangle = \frac{e^{2}}{4\pi\varepsilon_{0}} \iint |\phi_{1}(\mathbf{r}_{i})|^{2} |\phi_{2}(\mathbf{r}_{j})|^{2} \frac{1}{|\mathbf{r}_{i} - \mathbf{r}_{j}|} d^{3}r_{i}d^{3}r_{j} - \frac{e^{2}}{4\pi\varepsilon_{0}} \iint \phi_{1}^{*}(\mathbf{r}_{i})\phi_{2}^{*}(\mathbf{r}_{j}) \frac{1}{|\mathbf{r}_{i} - \mathbf{r}_{j}|} \phi_{2}(\mathbf{r}_{i})\phi_{1}(\mathbf{r}_{j})d^{3}r_{i}d^{3}r_{j}^{i}$$

A generalization for N-electrons can made by representing  $n_i$ quantum states by  $n_i$  and  $n_j$  in place of 1 and 2:

$$\langle \boldsymbol{\psi}_{a} \left| \boldsymbol{V}_{ij} \right| \boldsymbol{\psi}_{a} \rangle = \frac{e^{2}}{4\pi\varepsilon_{0}} \iint \left| \boldsymbol{\phi}_{n_{i}}(\mathbf{r}_{i}) \right|^{2} \left| \boldsymbol{\phi}_{n_{j}}(\mathbf{r}_{j}) \right|^{2} \frac{1}{\left| \mathbf{r}_{i} - \mathbf{r}_{j} \right|} d^{3}r_{i}d^{3}r_{j}$$

$$- \frac{e^{2}}{4\pi\varepsilon_{0}} \iint \boldsymbol{\phi}_{n_{i}}^{*}(\mathbf{r}_{i}) \boldsymbol{\phi}_{n_{j}}^{*}(\mathbf{r}_{j}) \frac{1}{\left| \mathbf{r}_{i} - \mathbf{r}_{j} \right|} \boldsymbol{\phi}_{n_{j}}(\mathbf{r}_{i}) \boldsymbol{\phi}_{n_{i}}(\mathbf{r}_{j}) d^{3}r_{i}d^{3}r_{j}$$

### Hartree-Fock Approximation

We then have,

$$\langle \Psi_{a} | H | \Psi_{a} \rangle = \sum_{i=1}^{N} \left[ \int \phi_{n_{i}}^{*} (\mathbf{r}_{i}) \left\{ -\frac{\hbar^{2}}{2m} \nabla_{i}^{2} + V_{ext}(\mathbf{r}_{i}) \right\} \phi_{n_{i}}(\mathbf{r}_{i}) d^{3}r_{i} \right. \\ \left. + \frac{1}{2} \sum_{i \neq j} \iint \left| \phi_{n_{i}}(\mathbf{r}_{i}) \right|^{2} \left| \phi_{n_{j}}(\mathbf{r}_{j}) \right|^{2} \frac{e^{2}}{4\pi\epsilon_{0} |\mathbf{r}_{i} - \mathbf{r}_{j}|} d^{3}r_{i} d^{3}r_{j} \\ \left. + \frac{1}{2} \sum_{i \neq j} \iint \left| \phi_{n_{i}}(\mathbf{r}_{i}) \phi_{n_{j}}(\mathbf{r}_{j}) \right|^{2} \frac{e^{2}}{4\pi\epsilon_{0} |\mathbf{r}_{i} - \mathbf{r}_{j}|} \phi_{n_{i}}(\mathbf{r}_{j}) \phi_{n_{i}}(\mathbf{r}_{j}) \\ \left. - \frac{1}{2} \sum_{i \neq j} \iint \phi_{n_{i}}^{*}(\mathbf{r}_{i}) \phi_{n_{j}}^{*}(\mathbf{r}_{j}) \frac{\phi_{n_{i}}^{*}(\cdot)}{4\pi\epsilon_{0} |\mathbf{r}_{i} - \mathbf{r}_{j}|} \phi_{n_{j}}(\mathbf{r}_{i}) \phi_{n_{i}}(\mathbf{r}_{j}) d^{3}r_{i} d^{3}r_{j} \right]$$
Minimization with respect to  $\phi_{n_{i}}^{*}(\mathbf{r}_{i})$ .

$$\left\{-\frac{\hbar^2}{2m}\nabla_i^2 + V_{ext}(\mathbf{r}_i)\right\}\phi_{n_i}(\mathbf{r}_i) + \frac{e^2}{4\pi\varepsilon_0}\left\{\sum_{j\neq i}\int \left|\phi_{n_j}(\mathbf{r}_j)\right|^2 \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}d^3r_j\right\}\phi_{n_i}(\mathbf{r}_i)$$

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$$-\frac{e^2}{4\pi\varepsilon_0}\left\{\sum_{j\neq i}\int\phi_{n_j}^*(\mathbf{r}_j)\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}\phi_{n_i}(\mathbf{r}_j)d^3r_j\phi_{n_j}(\mathbf{r}_i)\right\}=\varepsilon_{n_i}\phi_{n_i}(\mathbf{r}_i)$$

This equation is known as the Hartree-Fock equation. The third term on the left is originated from exchange interactions. 02/12/2022 Jinniu Ha U 'd r'

### Hartree-Fock Approximation

In 1930, Slater and V.A. Fock independently pointed out that the Hartree method did not respect the principle of antisymmetry of the wave function. The Hartree method used the Pauli exclusion principle in its older formulation, forbidding the presence of two electrons in the same quantum state. In 1935, Hartree reformulated the method to be more suitable for the purposes of calculation.



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Self-Consistent Field, with Exchange, for Beryllium

By D. R. HARTREE, F.R.S., and W. HARTREE

(Received February 25, 1935)





### The numerical code

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# RADIAL: A Fortran subroutine package for the solution of the radial Schrödinger and Dirac wave equations<sup>\*\*</sup>



Francesc Salvat<sup>\*</sup>, José M. Fernández-Varea Facultat de Física (FQA and ICC), Universitat de Barcelona, Diagonal 645, 08028 Barcelona, Catalonia, Spain



## radial: A Fortran subroutine package for the solution of radial Schrödinger and Dirac wave equations

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Contributors: Francesc Salvat, José M. Fernández-Varea

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For a system of N-electrons in a stationary state, this theory tries to avoid the complicated many-electron wave function by using electron density n(r), which is physically observable, measured, calculated, and easily visualized. The electron density to find a particle at  $or_n(r) = o(r) + o(r) + o(r)$  is given by

$$n(\mathbf{r}) = N \int d^3 r_2 \int d^3 r_3 \dots \int d^3 r_N \psi^*(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_N) \psi(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_N)$$

The Thomas-Fermi approach is semiclassical theory where certain ideas are borrowed from quantum mechanics.



- (I) Fermi statistics-all the states up to some maximum energy and momentum, say  $P_F$ , which may vary over the space are occupied (ii) The principle of uncertainty-every cell of phase space
- (of volume h<sup>3</sup>) can host up to two electrons with opposite spin directions.







Thus in the ground state volume occupied by the electrons  $$h^3$$  in the phase space would be

$$\frac{4\pi V}{3}p_F^3, \qquad V$$

where V is the volume of a system in real space. It is assumed that all electrons are accommodated up to the phase space sphere of radius  $p_F$ . Therefore the total number of electrons is

$$N = \left(\frac{4\pi V p_F^{3_F}}{3}\right) / \left(\frac{h^3}{2}\right) = \frac{8\pi V p_F^{3_F}}{3h^3}$$

and hence

$$n(\mathbf{r}) = \frac{N}{W} = \frac{8\pi p_{FF}^{33}}{3M^3} = \frac{p_{FF}^{33}}{3M^2 h^3}$$

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#### $\pi_F^3$ 周大學 Thomas-Fermi Theory V $3\pi^2\hbar^3$ 3h which gives $\pi F^{3}$ $p_F(\mathbf{r}) = \hbar k_F(\mathbf{r}), \text{ With } \mathcal{B}\mu(\mathbf{r}) = \mathfrak{B}\pi^2 n(\mathbf{r}) \Big\}^{1/3}$ The pF and kF are known as Fermi momentum and Fermi wave vector, respectively. It is rassumed there that $p_F$ and hence n(r) vary with space coordinates over the region. Assuming ${}^{n}$ that all electrons move as classical particles under the influence of common vegetential, the classical energy of fastest moving electrons is $E_{\max} = \frac{p_F^2(r)}{2m} + V(r)$ (T+U)where both kinetic and potential energy parts may $t(\mathbf{r})$ independently depend on r, and their $sum_{(1)}^{p} q$ remains constant. $t(\mathbf{r})$ d r $t(\mathbf{r})$ Jinniu Hu 02/12/2022
Thomas-Fermi Theory 2m 2mWe next take total energy  $(\underline{T}^{+}(\underline{v})) \circ f_{V}(\underline{t})$  he entire electrons distribution. With kinetic energy density  $t(\mathbf{r})$ , we write  $t(\mathbf{r}) \quad t(\mathbf{r}) \quad \mathbf{r} \quad T = \int t_{t}(\underline{\mathbf{r}}) d^{3}r$ .  $T = \int t_{t}(\underline{\mathbf{r}) d^{3}r$ .  $T = \int t_{t}(\underline{\mathbf{r}$ 

$$F(p)dp = \left(\frac{4\pi p^2 dp}{\frac{h^3}{2}}\right) = \frac{p^2 dp}{\pi^2 \hbar^3} \text{ when } p < p_F, \text{ zero otherwise.}$$

The t(r) at around r, when the classical expression for the kinet(r) of an electron is used, is:

$$t(\mathbf{r}) = \int_{0}^{p_{F}} \frac{p^{2}}{2m} F(p) dp = \frac{3\hbar^{2} (3)^{2/3} \pi^{4/3}}{10m} \{n(\mathbf{r})\}^{5/3}$$

# Thomas-Fermi\_Theory



r = 0 \_ \_

The total kinetic energy therefore is

 $t = C \qquad T = C_k \int n^{5/3}(\mathbf{r}) d^3 r = 2 \qquad 2/3 \pi^{4/3} = 10m$ where r  $C_k = \frac{3\hbar^2 (3)^{2/3} \pi^{4/3}}{10m}$ The potential renergy  $T_{at} \leftarrow \int_{S^2} d\mu e^{it} d\mu e^{it}$  interaction with the external field and electrostatic interaction of the  $7^{2}$  $Ze^2$ electron density with itselfZTherefore r = 00 r  $E \qquad T \qquad U = \int n(\mathbf{r}) V_{ext}(\mathbf{r}) d^3r + \frac{1}{2} \frac{e^2}{4\pi\epsilon} \int \int \frac{1}{3} \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \mathcal{U}(\mathbf{r}) \mathcal{U}(\mathbf{r}') \quad 3 \quad 3$  $Ze^2$ 

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 $\mathcal{I}^e$  Jinniu  $\mathcal{H}(\mathbf{u})^r = 0$ 

r = N

Ze

**Thomas-Fermi**  $\mathbf{T}_{l}$  $1 e^{-1}$  $n(\mathbf{r})n(\mathbf{r})$ 周 左e<sup>2</sup> 浮 n(**r**)n(**r**' Ze r = ()Ze The total energy of the system<sup>2</sup> is  $\mathbf{r} = 0$  $^{0}$  Z $e^{2}$  $E_{tot} = T + U = C_k \int n^{5/3}(\mathbf{r}) d^3r + \int n(\mathbf{r}) V_{ext}(\mathbf{r}) d^3r + \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \int \int \mathbf{r} \frac{\overline{n}(\mathbf{r}) n(\mathbf{r'})}{|\mathbf{r}|^2} d^3r d^3r' d^3r' n(\mathbf{r'})^0 = 0$ Next, we search for the electron density, ewhich (r)minimizes the total energy subject to the normalization condition  $\mu$ On introducing a Lagrange multiplier  $\mu$ , the method of the<sup> $\mu$ </sup> variational principle with respect to  $n(\mathbf{r})^{33}$  gives.  $\delta(E_{tot} - \mu N) = \int \left[\frac{5}{3}C_k n^{2/3}(\mathbf{r}) + V_{ext}(\mathbf{r}) + \frac{e^2}{4\pi\epsilon_0}\int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r' - \mu\right] \delta n(\mathbf{r}) d_1^3 \delta = 0$ which yields  $\mu = \frac{45}{3} C_k \left\{ n(\mathbf{r}) \right\}^{2/3} + V_{ext}(\mathbf{r}) + \frac{e_2^2}{4\pi\epsilon_0} \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \frac{d^3 r'}{d r}$ This equation is known as the Thomas-Fermi equation for determining the equilibrium distribution of the electron  $\partial B_N$ density. Jinnfu Hu 02/12/2022  $\partial E$ 

# Thomas-Fermi Theory for atom

Since the electrons cannot escape from the atom,  $\mu = 0$ 

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for an atom in equilibrium. Hence:  $^{0}_{3/2}$ 

$$\mathbf{r} = \left[ \frac{1}{5C_k} V_{eff}(\mathbf{r}) \right]^{3/2}$$

where

$$V_{eff}(\mathbf{r}) = V_{ext}(\mathbf{r}) + \frac{e^2}{e^4 \pi \varepsilon_0} \int_{\mathcal{H}} \frac{n(\mathbf{r'})}{|\mathbf{r'}|} \frac{d^3 r'}{dr'}$$

Because of spherical symmetry inside the atom, both (r) electron r density and  $V_{eff}$  (r) would be a function of r = f r f en(r)The electrostatic potential satisfy the Poisson's equation: 1 = 2 r r en(r)

$$\frac{1}{e} \nabla^2 V_{eff}(r) = -\frac{en(r)}{\varepsilon_0}$$
$$\Rightarrow \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dV_{eff}}{dr} \right) = -\frac{e^2 n(r)}{\varepsilon_0}$$

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# 周大學 Thomas-Fermi Theory for atom Therefore $\left[ \frac{1}{r + \frac{1}{r^2}} \frac{d}{dr} \left( r^2 \frac{dV_{eff}(r)}{dr} \right) = -\frac{e^2}{\varepsilon_0} \left[ -\frac{3}{5C_k} V_{eff}(\mathbf{r}) \right]^{3/2}$ $r \underbrace{\mathsf{It}}_{r \to 0} \underbrace{\mathsf{convenient}}_{Ze^2} \operatorname{to} \operatorname{i} \operatorname{Introduce}_{V(r)} = -\frac{Ze^2}{4\pi\varepsilon_0 r} \chi(r). \qquad V \xrightarrow{r}_{r \to 0} Ze^2 \qquad V \xrightarrow{r}_{eff} (r) = -\frac{Ze^2}{4\pi\varepsilon_0 r} \chi(r). \qquad V \xrightarrow{r}_{r \to 0} Ze^2 \qquad ()$ $\frac{3d_{2}^{2}\chi(r)}{dr^{2}} = \frac{e^{3}}{\varepsilon_{0}} \sqrt{\frac{Z}{4\pi\varepsilon_{0}}} \left\{\frac{3}{5C_{k}}\right\}^{3/2} \frac{\chi^{3/2}}{\sqrt{r}} \qquad ()$ 3/2 We then have: which on choosing $\begin{bmatrix} & r_{1/3} \\ b \\ r \end{bmatrix} = \begin{bmatrix} r_{1/3} \\ b \\ 4\pi \end{bmatrix} = \begin{bmatrix} r_{1/3} \\ b \\ 1/3 \end{bmatrix} = \begin{bmatrix} r_{1/3} \\ 2e \end{bmatrix} = 4\pi$ $x = \frac{3e}{b} \quad \text{with } b = \frac{5\varepsilon_0 \mathcal{O}_k}{3e^2} \left(\frac{Z}{4\pi}\right)^{1/3} \quad \frac{3e}{4\pi} \quad \frac{4\pi}{\left\{\begin{array}{c} \\ \end{array}\right\}^{3/2}} \quad \frac{d^2 \chi(x)}{dx^2} = \frac{\left\{\chi(x)\right\}^{3/2}}{\sqrt{x}}$ $\begin{cases} \end{cases}^{3/2} dx$ inniu Hu x 02/12/2022 $\gamma(\infty) \rightarrow \eta$ $\gamma(0) \rightarrow 1$



- The Schrödinger picture: the state vector,  $|\psi(t)\rangle$ , of a quantum system depends explicitly on time, while the observables (operators of physical characteristics) of the system are time-independent.
- The time evolution of the state vector is controlled by the Schrödinger equation

$$i\hbar \frac{\partial |\psi(t)\rangle}{\partial t} = \hat{H} |\psi(t)\rangle,$$

and can be represented in terms of a time evolution operator (propagator),  $U(t,t_o)$ , as

$$|\psi(t)\rangle = \hat{U}(t,t_0)|\psi(t_0)\rangle.$$



The condition of conservation of the norm of the wave function under this representation reads

> $\langle \boldsymbol{\psi}(t) | \boldsymbol{\psi}(t) \rangle = \langle \hat{U}(t,t_0) \boldsymbol{\psi}(t_0) | \hat{U}(t,t_0) \boldsymbol{\psi}(t_0) \rangle$ =  $\langle \boldsymbol{\psi}(t_0) | \hat{U}^{\dagger}(t,t_0) \hat{U}(t,t_0) | \boldsymbol{\psi}(t_0) \rangle = \langle \boldsymbol{\psi}(t_0) | \boldsymbol{\psi}(t_0) \rangle.$

- This requires the evolution operator, U(t,t<sub>o</sub>), to be unitary:  $\hat{U}^{\dagger}(t,t_0)\hat{U}(t,t_0) = \hat{U}(t,t_0)\hat{U}^{\dagger}(t,t_0) = \hat{I}.$
- In addition, the evolution operator also satisfies the following properties

$$\hat{U}(t,t) = \hat{I},$$
  

$$\hat{U}^{\dagger}(t,t_0) = \hat{U}^{-1}(t,t_0) = \hat{U}(t_0,t),$$
  

$$\hat{U}(t_k,t_j)\hat{U}(t_j,t_i) = \hat{U}(t_k,t_i), \quad t_k > t_j > t_i.$$

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- The propagator can be determined as follows,  $i\hbar \frac{\partial \hat{U}(t,t_0)}{\partial t} = \hat{H}\hat{U}(t,t_0).$ If the Hamiltonian, H, is time independent, its solution
- satisfying the initial condition,  $U(t_o, t_o) = I$ , can be written as  $\hat{U}(t, t_0) = e^{-\frac{i}{\hbar}(t-t_0)\hat{H}}$ .
- The wave function can be written as

$$|\Psi(t)\rangle = e^{-\frac{i}{\hbar}(t-t_0)\hat{H}}|\Psi(t_0)\rangle.$$

- We can expand the wave function  $\psi(q,0)$  into a series with
- respect to the eigenfunctions,  $\phi_m(q)$ , m = 1,2,3,..., of the

**Hamiltonian** 
$$\Psi(q,t) = \sum_{n=0}^{\infty} \frac{1}{n!} \left(\frac{-i\hat{H}}{\hbar}(t-t_0)\right)^n \sum_m c_m \phi_m$$

$$\Psi(q,t_0) = \sum_m c_m \phi_m(q), \qquad = \sum_m c_m \phi_m \sum_{n=0}^{\infty} \frac{1}{n!} \left(\frac{-iE_m^0}{\hbar}(t-t_0)\right)^n = \sum_m c_m \phi_m e^{-\frac{i}{\hbar}E_m^0(t-t_0)}.$$

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The Heisenberg picture: in this picture, the state vector, |  $\psi$ >, is time-independent, while the observables are timedependent. This is accomplished by defining the Heisenberg state vector,  $|\psi_{H}\rangle$ , as

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 $|\psi_H\rangle = \hat{U}^{\dagger}(t,t_0)|\psi(t)\rangle,$ 

With such a definition  $|\psi_{H}
angle$  turns out to be time-independent

$$|\psi_{H}\rangle = \hat{U}^{\dagger}(t,t_{0})|\psi(t)\rangle = \hat{U}^{-1}(t,t_{0})|\psi(t)\rangle = e^{\frac{i}{\hbar}(t-t_{0})\hat{H}}|\psi(t)\rangle = |\psi(t_{0})\rangle,$$

As a consequence, the state vector  $|\psi_{\rm H}\rangle$  gets frozen in time. This leads to

$$\frac{d|\psi_H\rangle}{dt}=0.$$



- U represents a unitary transformation of the state vector, physical properties of a quantum system in both the the Schrödinger and the Heisenberg pictures should be the same.
- For instance, consider the average value of time-independent observable, A<sub>s</sub>, in the Schrödinger picture

$$\langle \hat{A}_S \rangle = \langle \psi(t) | \hat{A}_S | \psi(t) \rangle = \langle \hat{U}(t, t_0) \psi_H | \hat{A}_S | \hat{U}(t, t_0) \psi_H \rangle$$

$$= \langle \Psi_H \left| \left( \hat{U}^{\dagger}(t,t_0) \hat{A}_S \hat{U}(t,t_0) \right) \right| \Psi_H \rangle$$

The requirement of the unchanged average value of A in both the pictures gives

$$\hat{A}_{H}(t) = \hat{U}^{\dagger}(t,t_{0})\hat{A}_{S}(t_{0})\hat{U}(t,t_{0}) = e^{\frac{i}{\hbar}(t-t_{0})\hat{H}}\hat{A}_{S}(t_{0})e^{-\frac{i}{\hbar}(t-t_{0})\hat{H}}.$$

The Heisenberg's equation of motion for an observable is obtained by simply differentiating it with respect to time

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$$\begin{aligned} \frac{d\hat{A}_{H}}{dt} &= \frac{i}{\hbar} e^{\frac{i}{\hbar}(t-t_{0})\hat{H}} \hat{H} \hat{A}_{S} e^{-\frac{i}{\hbar}(t-t_{0})\hat{H}} - \frac{i}{\hbar} e^{\frac{i}{\hbar}(t-t_{0})\hat{H}} \hat{A}_{S} \hat{H} e^{-\frac{i}{\hbar}(t-t_{0})\hat{H}} \\ &= \frac{i}{\hbar} \left( \left\{ e^{\frac{i}{\hbar}(t-t_{0})\hat{H}} \hat{H} e^{-\frac{i}{\hbar}(t-t_{0})\hat{H}} \right\} \left\{ e^{\frac{i}{\hbar}(t-t_{0})\hat{H}} \hat{A}_{S} e^{-\frac{i}{\hbar}(t-t_{0})\hat{H}} \right\} \\ &- \left\{ e^{\frac{i}{\hbar}(t-t_{0})\hat{H}} \hat{A}_{S} e^{-\frac{i}{\hbar}(t-t_{0})\hat{H}} \right\} \left\{ e^{\frac{i}{\hbar}(t-t_{0})\hat{H}} \hat{H} e^{-\frac{i}{\hbar}(t-t_{0})\hat{H}} \right\} \\ &= \frac{i}{\hbar} \left( \hat{H}_{H} \hat{A}_{H} - \hat{A}_{H} \hat{H}_{H} \right). \end{aligned}$$

Therefore, the Heisenberg's equation of motion can be written as

$$\frac{d\hat{A}_H}{dt} = \frac{1}{i\hbar} \left[ \hat{A}_H, \hat{H} \right]$$

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- Interaction picture: In this picture, both the state vector, |  $\psi_{I}(t)$ , and the observables depend explicitly on time.
- In the cases when the total Hamiltonian, H, can be separated into a time-independent part, H<sub>0</sub>, and a time-dependent part, W(t) (interaction Hamiltonian), the state vector,  $|\psi_{I}(t)\rangle$ , is defined through

$$|\psi_{I}\rangle = \hat{U}_{0}^{\dagger}(t,t_{0})|\psi(t)\rangle = \hat{U}_{0}^{-1}(t,t_{0})|\psi(t)\rangle \equiv e^{\frac{i}{\hbar}(t-t_{0})\hat{H}_{0}}|\psi(t)\rangle,$$

where  $|\psi(t)\rangle$  is the state vector in the Schrödinger picture. The equation of motion for the state vector is obtained as follows.



Defining an observable,  $A_{I}(t)$ , in the interaction picture by

$$\hat{A}_{I}(t) = e^{rac{i}{\hbar}(t-t_{0})\hat{H}_{0}}\hat{A}e^{-rac{i}{\hbar}(t-t_{0})\hat{H}_{0}},$$

where A is the corresponding observable in the Schrödinger's, and following the same calculations as in the case of Heisenberg's picture, we arrive at the following equation of motion for an observable in the interaction picture  $i\hbar \frac{d\hat{A}_I}{dt} = [\hat{A}_I, \hat{H}_0].$ 

We see that, in this picture, the time evolution of the state vector is governed by the time-dependent interaction Hamiltonian  $W_I(t)$  only, while the time variation of an observable is controlled only by the time-independent part.

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Differentiating  $|\psi_{I}
angle$  with respect to time, we obtain

$$\frac{\partial |\psi_I\rangle}{\partial t} = \frac{i}{\hbar} e^{\frac{i}{\hbar}(t-t_0)\hat{H}_0} \hat{H}_0 |\psi(t)\rangle + e^{\frac{i}{\hbar}(t-t_0)\hat{H}_0} \frac{\partial |\psi(t)\rangle}{\partial t}.$$

For  $|\psi(t)\rangle$  in the Schrödinger's picture, and a bit of algebra we obtain

$$i\hbar \frac{\partial |\psi_I(t)\rangle}{\partial t} = \hat{W}_I(t) |\psi_I(t)\rangle,$$

where

$$\hat{W}_{I}(t) = e^{\frac{i}{\hbar}(t-t_{0})\hat{H}_{0}}\hat{W}(t)e^{-\frac{i}{\hbar}(t-t_{0})\hat{H}_{0}}$$

is the time-dependent part of the total Hamiltonian in the interaction picture.

The time independence of the Hamiltonian allows to us to factorize the wave function into space- and timedependent parts  $_{0}\psi$   $_{0}\psi$   $_{1}\psi$   $_{2}\psi$   $_{1}\psi$   $_{2}\psi$   $_{1}\psi$   $_{2}\psi$   $_{1}\psi$   $_{2}\psi$   $_{1}\psi$   $_{2}\psi$   $_$ 

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### and

$$\begin{bmatrix} -\frac{\hbar^2}{2m}\nabla_2^2 + V(\mathbf{r}) \\ V \end{bmatrix} \phi(\mathbf{r}) = E\phi(\mathbf{r}) \\ E \quad ()$$

When, the Hamiltonian is time-dependent, factorization of E the wave function into space- and time-dependent parts V(r) is not possible and hence the Schrödinger picture is inadequate to describe the system.

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The approach adopted by us is as follows. Let us say  $H_{\circ}$  satisfies the Heigenvalue equation:

$$H_0|\phi_n\rangle = E_n|\phi_n\rangle$$

En and  $\phi_n$  are the lenergy eigenvalue and eigenstate of the nth state of the system in the  $\phi_n$  because of  $E_n$   $E_n^{(0)}$ perturbation  $\phi_n$   $\phi$ 

The eigenstate  $\oint_n$  can be taken as basis vectors of Hilbert space to write  $\sum_{n=1}^{n} a_n = n$  c(0)

周大學 Exactly Solvable Time-dependents In the absence  $\rho f^{n} H_{1}(r,t)$ , we are dealing with stationary state problems and hence we have  $i \in t$  $\psi(\mathbf{r},t) = \sum_{\mathbf{r},n} (0) e^{-\frac{iE_n t}{\hbar}} \phi_n(\mathbf{r})$ Now, let us consider the situation where initially, in the absence of  $H_1(\mathbf{r},t)$ , only one of the eigenstate  $H_1(\mathbf{r},t)$  is populated. But as time goes on and  $H_1(r,t)$  is turned on, states other (it han  $\phi_i$  get populated. We can expect that  $\psi(\mathbf{r},t)$  is still represented in the same form as above equation, provided  $c_n$  is made time-dependent. We therefore write,

$$|\Psi(t)\rangle = \sum_{n} c_n(t) e^{\frac{iE}{\hbar} \frac{t_{iE_nt}}{\hbar}} |\phi_n\rangle$$

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Jinniu  $H_{u(t)}$ 



Exactly Solvable Time-dependent



Note that in this photoedure, time-dependence of  $c_n(t)$  is solely arising due to  $H_1(r,t)$  and it must go to  $c_n(0)_{H(r,t)=H_0(r)+H_1(r,t)}^{C(t)}$ whenever  $H_1(r,t) = 0$ .

The time-dependence  $odt c_n(t)$  is thus determined from the Schrödinger equation having the Hamiltonian H(r,t)=H<sub>0</sub>(r)

 $+H_{1}(r,t),$ 

$$i\hbar \frac{\partial}{\partial t} \sum_{n} c_{n}(t) e^{-\frac{iE_{n}t}{\hbar}} |\phi_{n}\rangle = (H_{0} + H_{1}) \sum_{n} c_{n}(t) e^{-\frac{iE_{n}t}{\hbar}} |\phi_{n}\rangle$$

$$\Rightarrow i\hbar \sum_{n} \dot{c}_{n}(t) e^{-\frac{iE_{n}t}{\hbar}} |\phi_{n}\rangle + \sum_{n} E_{n} c_{n}(t) e^{-\frac{iE_{n}t}{\hbar}} |\phi_{n}\rangle$$

$$= \sum_{n} E_{n} c_{n}(t) e^{-\frac{iE_{n}t}{\hbar}} |\phi_{n}\rangle + H_{1}(\mathbf{r}, t) \sum_{n} c_{n}(t) e^{-\frac{iE_{n}t}{\hbar}} |\phi_{n}\rangle$$

$$\Rightarrow i\hbar \sum_{n} \dot{c}_{n}(t) e^{-\frac{iE_{n}t}{\hbar}} |\phi_{n}\rangle = H_{1}(\mathbf{r}, t) \sum_{n} c_{n}(t) e^{-\frac{iE_{n}t}{\hbar}} |\phi_{n}\rangle$$

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## **Exactly Solvable Time-dependent**

On taking the inner product with

 $\omega = \frac{(E_m - E_n)}{\hbar}$ 

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### and the defining



iEmt

 $\langle \phi_m | e^{-\hbar}$ 

Exactly Solvable Time-dependent  $(t) = \phi_m$   $(t) = \phi_$ 

### We thus obtained a matrix equation,



- which yields coupled equations that are solved to find  $c_1(t)$ ,  $c_1(t), c_2(t), \dots, c_n(t), \dots, c_$
- Note that we have not used any approximation until now and hence all treatments are exact. Exactly solvable problems with time-dependent potentials are rather rare.

# A two-state system problem with sinusoidal perturbing potential is described as follows, $-iE_{2}t$

$$\left|\psi\right\rangle = c_{1}(t)e^{\frac{-i\underline{\hbar}_{1t}}{\hbar}}\left|\phi_{1}\right\rangle + c_{2}^{2}(t)e^{\frac{-i\underline{\hbar}_{2t}}{\hbar}}\left|\phi_{2}^{2}\right\rangle$$

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 $= \oint_{H_0} \frac{\phi}{E_1} + E \oint_{D_1} \frac{\phi}{E_2} > H_0 = E_1 \left| \phi_1 \right\rangle \left\langle \phi_1 \right| + E_2 \left| \phi_2 \right\rangle \left\langle \phi_2 \right|, \text{ with } E_2 > E_1$ 

#### and

$$H_{1} = \gamma e_{i\omega t}^{i\omega t} |\phi_{1}\rangle \langle \phi_{2}| + \gamma e_{-i\omega t}^{-i\omega t} |\phi_{2}\rangle \langle \phi_{1}|$$
  
=  $\gamma \phi \phi_{2} + \gamma \phi_{2} \phi_{2}$ 

where  $\gamma$  and  $\omega$  are real positive. We thus have timedependent perturbing potential that connects the two states and the transition between two states takes place.



Periodic external field  $\omega d^{2e}(t)$   $d^{(E_{1}-E_{2})}$   $\hbar e^{i} t^{c}$   $\omega d^{2e}(t)$  d (t) f (

This is a standard second order differential equation. We observe that the discount of the solve it with the disc of a trial solution,

Therefore,  $C_2(t) = c_2(0)e^{i\Omega t}$ ,  $C_2(t) = c_2(0)e^{i\Omega t}$ ,

$$\begin{bmatrix} \Omega^2 + \Omega(\omega - \omega_{21}) - \left(\frac{\gamma}{\hbar}\right)^2 \end{bmatrix} \equiv 0 2^{-1/2}$$

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whose solution is

$$\Omega = -\frac{1}{2}(\omega - \omega_{21}) \pm \left\{ \left(\frac{\omega - \omega_{21}}{2}\right)^2 + \left(\frac{\gamma^2}{\hbar}\right)^2 \right\}^{\frac{1}{2}}$$

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### Periodic external field

Periodic external field  
Finally, 
$$c_{c} t_{t} = \int_{c_{c}(t) = e^{-i\frac{(\omega - \omega_{21})^{2}}{2}} \left[ Ae^{i\frac{(\omega - \omega_{21})^{2} + (\frac{1}{R})^{2}}{2}} \right] \right]$$
  
if initiating at t = 0 only the lower state  $c_{c}(t)$  is populated so  
 $A = -\frac{1}{e^{-i\frac{(\omega - \omega_{21})^{2}}{2}} \left[ (t) = \gamma_{t}^{t=0} \right]$   
So,  
 $A = -\frac{t}{\left\{ \hbar^{2} (\omega - \omega_{21})^{2} + 4\gamma_{t}^{2} \right\}^{1/2}}$   
The probability that both the states  $\phi_{1}$  and  $\phi_{2}$  are  
 $populated$  at later time t is then give by  
 $|c_{2}(t)|^{2} = \frac{\gamma^{2}}{\left\{ \hbar^{2} \left( \frac{(\omega - \omega_{21})^{2}}{2} + \gamma^{2} \right\}^{2}} \sin^{2} \left\{ \left[ \sqrt{\left( \frac{(\omega - \omega_{21})^{2} + \left( \frac{\gamma}{L} \right)^{2}}{2} + \left( \frac{\gamma}{L} \right)^{2} \right]^{2}} \right\}$ 

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which is known as the Resonance condition.

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# Periodic external field

 $\omega \neq \omega_{21}$ 

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The  $|c_2(t)|^2$  and  $|c_1(t)|^2$  are plotted as the function of t at  $\omega = \omega_{21}$  (resonance condition) in



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Time-dependent Perturbation Theory

Except for a few problems such as two state timedependent systems, the exact solution to differential equations that determine  $c_n$  (t) is not possible.

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Similar to the case of time-independent perturbation theory, we include the small dimensionless parameter  $\lambda$  to write the Hamiltonian  $\lambda$   $\lambda$   $\lambda$   $H = H_0 + \lambda H_1$ and expand the  $(2n + 1)^{(1)}$  in the rest of  $\lambda$  as follows:....  $H = H_0 +$  $H = H_0$  $2^{(2)}() + \lambda^{3} (3)() + \sum_{n=1}^{\infty} c_n(t) = c_n^{(0)}(t) + \lambda c_n^{(1)}(t) + \lambda^2 c_n^{(2)}(t) + \lambda^3 q_{\eta_1}^{(3)}(t) + \sum_{n=1}^{\infty} c_n^{(3)}(t) + \sum_{n=1$ Therefore,  $H_1$  $\lambda H_1$  $H_1$  $\lambda(\mathbf{P}_{t}, t) + \lambda \dot{c}_{m}^{(1)}(t) + \lambda^{2} \dot{c}_{m}^{(2)}(t) + \dots$  $=\frac{1}{i\hbar}\sum h_{mn}(t)\Big\{\lambda c_{n}^{(0)}(t)+\lambda^{2}c_{n}^{(1)}(t)+\lambda^{3}c_{n}^{(2)}(t)++\ldots\Big\}e^{i\omega_{mn}t}\Big\}$ Jinniu Hu 02/12/2022 ז *ו* ו *i* ו

Time-dependent Perturbation Theory

$$H_0^{(0)}(t) = \frac{1}{i\hbar} \sum_n h_{mn}(t) c_n^{(0)}(t) e^{i\omega_{mn}t}$$

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$$\frac{dc_m^{(2)}(t)}{(t)^{dt}} = \frac{1}{i\hbar} \sum_n h_{mn}(t) c_n^{(1)}(t) e^{i\omega_{mn}t}$$

The first order contribution to  $c_m$  (t) is

$$c_m^{(1)}(t) \equiv \frac{c \mathbf{1}^{(0)}}{H_{d\hbar}} \int \sum_n h_{mn}(t') c_n^{(0)}(t') e^{i\omega_{mn}t'} dt'$$

If the system initially at t = 0 is in only one unperturbed state  $\phi_n$  then  $c_n^{(0)}$  is non-zero (equal to 1) only for one value of n belonging to  $\phi_n$ , and it is zero for all other values of m.  $c^{(1)}$  t  $d^{(1)}$  Jirriniu Hu



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Let us consider a system initially in the state of  $\phi_n$ perturbed by a periodic potential that is described by  $H_1(\mathbf{r},t) = 2H_1(\mathbf{r})\cos(\omega t) = H_1(\mathbf{r})\left\{e^{i\omega t} + e^{-i\omega t}\right\}$ An example of this is an atom or a molecule exposed to electromagnetic radiation (harmonic perturbation). The

electromagnetic radiation (harmonic perturbation). The probability amplitude for an atom in the initial state  $\phi_n$  to be in state  $\phi_m$  after (time t)  $h_{mn}(t') = H_{mn}(e^{i\omega t'} + e^{-i\omega t'})$ , where  $H_{mn} = \langle \phi_m | H_1(\mathbf{r}) | \phi_n \rangle$ 

We have

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$$c_{m}^{(1)}(t) = \frac{H_{mn}}{i\hbar} \int_{0}^{t} \left( e^{i(\omega + \omega_{mn})t'} + e^{-i(\omega - \omega_{mn})t'} \right) dt'$$
  

$$\Rightarrow c_{m}^{(1)}(t) = H_{mn} \left[ \frac{e^{\left(-i(\omega - \omega_{mn})t - 1\right)}}{\hbar(\omega - \omega_{mn})} - \frac{e^{i(\omega + \omega_{mn})t}}{\hbar(\omega + \omega_{mn})} \right]$$
  

$$= 1$$
  
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The first term on the right-hand side represents absorption, while the second corresponds to stimulated\_ emission. Since both absorption and stimulated emission cannot take place simultaneously, only one term is to be discussed at a time. We retain the first term for further discussions and obtain:

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$$c_m^{(1)}(t) = H_{mn} \frac{e^{-i(\omega - \omega_{mn})t} - 1}{\hbar(\omega - \omega_{mn})}$$
$$= \frac{H_{mn}}{\hbar(\omega - \omega_{mn})} e^{\frac{i(\omega_{mn} - \omega)t}{2}} \left[ e^{\frac{i(\omega_{mn} - \omega)t}{2}} - e^{\frac{-i(\omega_{mn} - \omega)t}{2}} \right]$$
$$= \frac{2iH_{mn}}{\hbar(\omega - \omega_{mn})} e^{\frac{i(\omega_{mn} - \omega)t}{2}} \sin\left\{\frac{(\omega_{mn} - \omega)t}{2}\right\}$$

# Transition Probability

If the system was in the  $\phi_n$  state initially at t=0, then the probability to find the system in the state  $\phi_m$  after time t is given by  $t^t$ 

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$$t = 0 \qquad P_{n \to m}(t) = \left| c_m^{(1)}(t) \right|^2 = \frac{\left| H_{mn}^2 \right|^2}{\hbar^2 \left( \frac{\omega_{mn} - \omega}{2 \ 2} \right)^2} \operatorname{sinf}^{\varrho} \left\{ \frac{(\omega_{mn} - \omega)t}{2 \ 2} \right\}$$

(*t*)

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### **Transition Probability**



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A<sup>P</sup> central peak (has the largest height. As t increases, the height of the central peak enhances as  $t_t^2$  while its width decrease as 1/t. For  $t^2 \rightarrow \infty$ , one expects that the functions:

$$\frac{\sin^{2}\alpha t}{\alpha^{\text{M}}} \to \pi t \delta(\alpha)$$

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We next consider the transitions from one of the initial discrete states to a final state that is part of a continuum, with density of states  $\rho(E_m)$ .

The probability of transition between discrete states exhibits periodic dependence in time. But, if the final state is part of a continuum, an integral over all final states is required to get a resultant transition probability. A transition rate is associated with such a probability function. The final transition rate is given by Fermi's Golden Rule. An approximation to the sum of transition probabilities

over final states is given by the integral

$$P(t)\sum_{m}\sum_{m}P_{n\to m}(t)\int \int P_{n\to m}(t)\rho(E_{m}^{m})vdE_{m}^{m}$$

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which gives

$$P(t_{P-t}^{P}\int \frac{H_{mn}^{2}\sin^{2}(\alpha t)}{\hbar} \alpha^{2} \alpha \rho(E_{m}) dE_{m}^{E} m_{m}^{m}$$

In this range of energy,  $H_{mn}^2$  and  $\rho(E_m)$  almost remain the same, and they are treated independent of  $energy_{mn}^2 rgy_{(E_m)}$  in the continuum of states. We thus have

$$P(t) = \frac{|H_{mn}|^2}{\hbar \frac{\hbar^2}{n}} \rho_m(E_m) \int \frac{\sin^2(\alpha t)}{\alpha \alpha^2} dE_m$$

## Transition Probability <sub>2</sub>

mn

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Note that

$$\alpha = \frac{\frac{mn_2}{2} - \omega}{2} = \frac{E_m - E_n}{2\hbar} - \frac{\omega}{2}$$
$$\Rightarrow dE(m = 2\hbar d\alpha)$$

Since the integral is contributed by a very small energy range, our answer will not be changed even if the limit of integration over  $\alpha_h$  is extended to  $\pm_h^\infty$   $\mathcal{HWe}^+$  (therefore have  $-\infty$ 

$$P(t) = \frac{2|H_{mn}|^2}{\hbar} \rho(E_m) \int_{-\infty}^{\infty} \frac{\sin^2(\alpha t)}{\alpha^2} d\alpha = \frac{2\pi}{\hbar} t |H_{mn}^{H_{n}2n} \rho(E_m^{(E_m)})$$

where we made use of  $=\pi$ 

$$\int_{-\infty}^{\infty} \left(\frac{\sin x}{x}\right)^2 dx = \pi \pi \qquad t \qquad t$$

$$t^2 \qquad 1/t$$

t t

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t

+ t

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$\frac{\hbar}{\text{Transition}} \text{Probability}^{\hbar}$ 

Note that the total transition probability is proportional to T FOR LARGE VALUES of t. We restricted the integral to the central peak only, which yields our answer 90% correct. Inclusion of more peaks from to the left and  $right^2$  of the central  $\frac{d}{dt}$  eak timproves accuracy further. The probability of transition per unit time P(t)/t, also termed the transition rate is  $w_{n \to m}(t) = \frac{P_{n \to m}(t)}{t} = \frac{\pi |H_{mn}|^2}{t^2} \delta(\alpha)$ 

 $II_{mn}$  ( $L_m$ )

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This equation is known as Fermi's Golden Rule. It shows that total transition probability is independent of time.  $w \rightarrow \rho(E)$ 02/12/2022 Jinniu Hu

## Exercise

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1. A delta function bump  $H_1 = \alpha \delta(x - a/2)$  is introduced at the center of the infinite potential well of width a , with walls at x = 0 and x = a . Calculate the first order correction to the allowed energies and wave function.



## Exercise

1. A delta function bump  $H_1 = \alpha \delta(x - a/2)$  is introduced at the center of the infinite potential well of width a , with walls at x = 0 and x = a. Calculate the first order =  $\alpha\delta(x-a/2)$  ion to the allowed energies and wave function. x = 0 x = 0 x = aSolution: The first order corrections to the allowed energies are given by  $E_n^{(1)} = \left\langle \boldsymbol{\Psi}_n^{(0)} \middle| H_1 \middle| \boldsymbol{\Psi}_n^{(0)} \right\rangle. \quad H \quad E$ Η  $\psi^{(0)}x = a \qquad \psi^{(0)}x = a \qquad x = 0 \qquad x = 0 \qquad x = 0 \qquad x = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right). \qquad a \qquad a$ 

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Therefore, n  $E_n^{(1)} = \frac{2}{a} \int_0^a \left( \sin\left(\frac{n\pi}{a}x\right) \right)^2 \alpha \delta(x - a/2) dx$   $= \frac{2\alpha}{a} \left( \sin\left(\frac{n\pi}{2}x\right) \right)^2$ 

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