# Advanced Physical Chemistry 

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# Quantum Chemistry 

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## Emphasis

## Hartree-Fock method <br> Concepts <br> Hands-on experience

Text Book

## "Quantum Chemistry", 4th Ed. Ira N. Levine

http://yangtze.hku.hk/lecture/chem3504-3.ppt

## Beginning of Computational Chemistry

In 1929, Dirac declared, "The underlying physical laws necessary for the mathematical theory of ...the whole of chemistry are thus completely know, and the difficulty is only that the exact application of these laws leads to equations much ton comnlicated to be soluble."


## Quantum Chemistry Methods

- Ab initio molecular orbital methods
- Semiempirical molecular orbital methods
- Density functional method


## Schrödinger Equation

## $\mathbf{H} \psi=\mathbf{E} \psi$

## Wavefunction

$$
\begin{aligned}
& \text { Hamiltonian } \\
& \begin{array}{l}
H=\sum_{\alpha}\left(-\mathbf{h}^{2} / 2 \mathbf{m}_{\alpha}\right) \nabla_{\alpha}^{2}-\left(\mathbf{h}^{2} / 2 \mathbf{m}_{\mathrm{e}}\right) \sum_{\mathrm{i}} \nabla_{\mathrm{i}}^{2} \\
\quad+\sum_{\alpha} \sum_{\beta} \mathbf{Z}_{\alpha} \mathbf{Z}_{\beta} \mathbf{e}^{2} / \mathbf{r}_{\alpha \beta}-\sum_{\mathrm{i}} \sum_{\alpha} \mathbf{Z}_{\alpha} \mathbf{e}^{2} / \mathbf{r}_{\mathrm{i}_{\alpha}} \\
\quad+\sum_{\mathrm{i}} \sum_{\mathrm{j}} \mathbf{e}^{2} / \mathbf{r}_{\mathrm{ij}}
\end{array}
\end{aligned}
$$

## Energy

## Contents

1. Variation Method
2. Hartree-Fock Self-Consistent Field Method

## The Variation Method

## The variation theorem

Consider a system whose Hamiltonian operator $H$ is time independent and whose lowest-energy eigenvalue is $E_{l}$. If $\phi$ is any normalized, wellbehaved function that satisfies the boundary conditions of the problem, then

$$
\int \phi^{*} H \phi \mathrm{~d} \tau \geq E_{1}
$$

## Proof:

Expand $\phi$ in the basis set $\left\{\psi_{k}\right\}$

$$
\phi=\Sigma_{\mathrm{k}} \alpha_{\mathrm{k}} \psi_{\mathrm{k}}
$$

where

$$
\begin{aligned}
& \left\{\alpha_{\mathrm{k}}\right\} \text { are coefficients } \\
& H \psi_{\mathrm{k}}=E_{\mathrm{k}} \psi_{\mathrm{k}}
\end{aligned}
$$

then

$$
\begin{aligned}
\int \phi^{*} H \phi \mathrm{~d} \tau & =\Sigma_{\mathrm{k}} \Sigma_{\mathrm{j}} \alpha_{\mathrm{k}}{ }^{*} \alpha_{\mathrm{j}} \mathrm{E}_{\mathrm{j}} \delta_{\mathrm{kj}} \\
& =\Sigma_{\mathrm{k}}\left|\alpha_{\mathrm{k}}\right|^{2} E_{k} \geq E_{1} \Sigma_{\mathrm{k}}\left|\alpha_{\mathrm{k}}\right|^{2}=E_{1}
\end{aligned}
$$

Since is normalized, $\int \phi^{*} \phi \mathrm{~d} \tau=\Sigma_{\mathrm{k}}\left|\alpha_{\mathrm{k}}\right|^{2}=1$
i. $\phi$ : trial function is used to evaluate the upper limit of ground state energy $\boldsymbol{E}_{\mathbf{1}}$
ii. $\phi=$ ground state wave function, $\int \phi^{*} \boldsymbol{H} \boldsymbol{\phi} \mathrm{~d} \tau=\boldsymbol{E}_{1}$
iii. optimize paramemters in $\phi$ by minimizing

$$
\int \phi^{*} H \phi d \tau / \int \phi^{*} \phi d \tau
$$

## Application to a particle in a box of infinite depth



Requirements for the trial wave function:
i. zero at boundary;
ii. smoothness $\Rightarrow$ a maximum in the center.

Trial wave function: $\phi=\mathrm{x}(1-\mathrm{x})$

$$
\begin{aligned}
\int \phi^{*} H \phi d x & =-\left(h^{2} / 8 \pi^{2} m\right) \int\left(\left(x-x^{2}\right) d^{2}\left(l \mathbf{x}-x^{2}\right) / d x^{2} d x\right. \\
& =h^{2} /\left(4 \pi^{2} \mathbf{m}\right) \int\left(\mathbf{x}^{2}-I x\right) d x \\
& =h^{2} \beta^{2} /\left(24 \pi^{2} m\right)
\end{aligned}
$$

$$
\int \phi^{*} \phi d x=\int x^{2}(I-x)^{2} d x=F / 30
$$

$$
\mathrm{E}_{\phi}=5 \mathrm{~h}^{2} /\left(4 \pi^{2} \mathcal{P} \mathrm{~m}\right) \geq \mathrm{h}^{2} /(8 \mathrm{~m} \mathcal{P})=\mathrm{E}_{1}
$$

## Variational Method

(1) Construct a wave function $\phi\left(\mathrm{c}_{1}, \mathrm{c}_{2}, \bullet \bullet \bullet, \mathrm{c}_{\mathrm{m}}\right)$
(2) Calculate the energy of $\phi$ :

$$
\mathrm{E}_{\phi} \equiv \mathrm{E}_{\phi}\left(\mathrm{c}_{1}, \mathrm{c}_{2}, \bullet \bullet \bullet, \mathrm{c}_{\mathrm{m}}\right)
$$

(3) Choose $\left\{\mathrm{c}_{\mathrm{j}}^{*}\right\}(\mathrm{i}=1,2, \bullet \bullet \bullet, \mathrm{~m})$ so that $\mathrm{E}_{\phi}$ is minimum

## Example: one-dimensional harmonic oscillator

Potential: $V(x)=(1 / 2) k x^{2}=(1 / 2) m \omega^{2} x^{2}=2 \pi^{2} m v^{2} x^{2}$
Trial wave function for the ground state:

$$
\phi(x)=\exp \left(-c x^{2}\right)
$$

$$
\int \phi^{*} H \phi d x=-\left(h^{2} / 8 \pi^{2} m\right) \int \exp \left(-c x^{2}\right) d^{2}\left[\exp \left(-c x^{2}\right)\right] / d x^{2} d x
$$

$$
+2 \pi^{2} m v^{2} \int x^{2} \exp \left(-2 c x^{2}\right) d x
$$

$$
=\left(\mathbf{h}^{2} / 4 \pi^{2} \mathrm{~m}\right)(\pi \mathrm{c} / 8)^{1 / 2}+\pi^{2} \mathrm{~m} v^{2}\left(\pi / 8 \mathrm{c}^{3}\right)^{1 / 2}
$$

$$
\int \phi^{*} \phi d x=\int \exp \left(-2 c x^{2}\right) d x=(\pi / 2)^{1 / 2} c^{-1 / 2}
$$

$$
\mathbf{E}_{\phi}=\mathbf{W}=\left(\mathbf{h}^{2} / 8 \pi^{2} \mathbf{m}\right) \mathbf{c}+\left(\pi^{2} / 2\right) m v^{2} / \mathbf{c}
$$

## $h^{2} / 8 \pi^{2} m-\left(\pi^{2} / 2\right) m v^{2} c^{-2}$

## $=2 \pi^{2} v \mathrm{~m} / \mathrm{h}$

## To minimize W,

## $0=\mathrm{dW} / \mathrm{dc}=$

$$
W=(1 / 2) h \nu
$$

## Extension of Variation Method



For a wave function $\phi$ which is orthogonal to the ground state wave function $\psi_{1}$, i.e.

$$
\begin{array}{r}
\int \mathrm{d} \tau \phi^{*} \psi_{1}=0 \\
E_{\phi}=\int \mathrm{d} \tau \phi^{*} H \phi / \int \mathrm{d} \tau \phi^{*} \phi \geq E_{2}
\end{array}
$$

$$
\int \mathrm{d} \tau \phi^{*} \psi_{1}=0
$$

$$
\begin{aligned}
& \sum_{\mathrm{k}=2}\left|\mathrm{a}_{\mathrm{k}}\right|^{2} E_{\mathrm{k}} / \sum_{\mathrm{k}=2}\left|\mathrm{a}_{\mathrm{k}}\right|^{2} \\
& \sum_{\mathrm{k}=2}\left|\mathrm{a}_{\mathrm{k}}\right|^{2} E_{2} / \sum_{\mathrm{k}=2}\left|\mathrm{a}_{\mathrm{k}}\right|^{2}=
\end{aligned}
$$

## The trial wave function $\phi$ :

$$
\phi=\sum_{\mathrm{k}=1} \mathrm{a}_{\mathrm{k}} \psi_{\mathrm{k}}
$$

$\int \mathrm{d} \tau \phi^{*} \psi_{1}=\left|\mathrm{a}_{1}\right|^{2}=0$ $E_{\phi}=\int \mathrm{d} \tau \phi^{*} H \phi / \int \mathrm{d} \tau \phi^{*} \phi=$
$E_{2}$


## $\left.{ }^{2} H_{22}\right)$

$H_{11}+2 \mathrm{c}_{1} \mathrm{c}_{2} H_{12}+\mathrm{c}_{2}^{2} H_{22}$

## Application to $\mathbf{H}_{2}{ }^{+}$


$\mathrm{W}=\int \phi^{*} H \phi \mathrm{~d} \tau / \int \phi^{*} \phi \mathrm{~d} \tau$

$$
\begin{aligned}
= & \left(\mathrm{c}_{1}{ }^{2} H_{11}+2 \mathrm{c}_{1} \mathrm{c}_{2} H_{12}+\mathrm{c}\right. \\
& /\left(\mathrm{c}_{1}{ }^{2}+2 \mathrm{c}_{1} \mathrm{c}_{2} S+\mathrm{c}_{2}^{2}\right)
\end{aligned}
$$

$\mathrm{W}\left(\mathrm{c}_{1}^{2}+2 \mathrm{c}_{1} \mathrm{c}_{2} S+\mathrm{c}_{2}^{2}\right)=\mathrm{c}_{1}^{2}$

Partial derivative with respect to $\mathrm{c}_{1}\left(\partial \mathrm{~W} / \partial \mathrm{c}_{1}=0\right)$ :
$\mathrm{W}\left(\mathrm{c}_{1}+S \mathrm{c}_{2}\right)=\mathrm{c}_{1} H_{11}+\mathrm{c}_{2} H_{12}$
Partial derivative with respect to $\mathrm{c}_{2}\left(\partial \mathrm{~W} / \partial \mathrm{c}_{2}=0\right)$ :

$$
\mathrm{W}\left(S \mathrm{c}_{1}+\mathrm{c}_{2}\right)=\mathrm{c}_{1} H_{12}+\mathrm{c}_{2} H_{22}
$$

$$
\left(H_{11}-\mathrm{W}\right) \mathrm{c}_{1}+\left(H_{12}-S \mathrm{~W}\right) \mathrm{c}_{2}=0
$$

$$
\left(H_{12}-S \mathrm{~W}\right) \mathrm{c}_{1}+\left(H_{22}-\mathrm{W}\right) \mathrm{c}_{2}=0
$$

## To have nontrivial solution:

$$
\left.\begin{array}{ll}
H_{11}-\mathrm{W} & H_{12}-S \mathrm{~W} \\
H_{12}-S \mathrm{~W} & H_{22}-\mathrm{W}
\end{array} \right\rvert\,=0
$$

For $\mathrm{H}_{2}^{+}, H_{11}=H_{22} ; H_{12}<0$.

Ground State: $E_{\mathrm{g}}=\mathrm{W}_{1}=\left(H_{11}+H_{12}\right) /(1+S)$

$$
\phi_{1}=\left(\psi_{1}+\psi_{2}\right) / \sqrt{2}(1+\mathrm{S})^{1 / 2} \quad \text { bonding orbital }
$$

Excited State: $E_{\mathrm{e}}=\mathrm{W}_{2}=\left(H_{11}-H_{12}\right) /(1-S)$

$$
\phi_{2}=\left(\psi_{1}-\psi_{2}\right) / \sqrt{2}(1-\mathrm{S})^{1 / 2} \text { Anti-bonding orbital }
$$

## $76 \mathrm{eV}, R_{\mathrm{e}}=1.32 A$

## $.79 \mathrm{eV}, R_{\mathrm{e}}=1.06 A$

## Results: $D_{\mathrm{e}}=1$

## Exact: <br> 

## Further Improvements

Optimization of 1s orbitals
$\mathrm{H} \quad \pi^{-1 / 2} \exp (-r)$
$\mathrm{He}^{+} \quad 2^{3 / 2} \pi^{-1 / 2} \exp (-2 r)$
Trial wave function: $k^{3 / 2} \pi^{-1 / 2} \exp (-k r)$

$$
E_{\mathrm{g}}=\mathrm{W}_{1}(k, R)
$$

at each $R$, choose $k$ so that $\partial \mathrm{W}_{1} / \partial k=0$
Results:
$D_{\mathrm{e}}=2.36 \mathrm{eV}, R_{\mathrm{e}}=1.06 \mathrm{~A}$

Inclusion of other atomic orbitals


Resutls: $D_{\mathrm{e}}=2.73 \mathrm{eV}, R_{\mathrm{e}}=1.06 \mathrm{~A}$

## Linear Equations

1. two linear equations for two unknown, $x_{1}$ and $x_{2}$
$\mathrm{a}_{11} x_{1}+\mathrm{a}_{12} x_{2}=\mathrm{b}_{1}$
$\mathrm{a}_{21} x_{1}+\mathrm{a}_{22} x_{2}=\mathrm{b}_{2}$
$\left(\mathrm{a}_{11} \mathrm{a}_{22}-\mathrm{a}_{12} \mathrm{a}_{21}\right) x_{1}=\mathrm{b}_{1} \mathrm{a}_{22}-\mathrm{b}_{2} \mathrm{a}_{12}$
$\left(\mathrm{a}_{11} \mathrm{a}_{22}-\mathrm{a}_{12} \mathrm{a}_{21}\right) x_{2}=\mathrm{b}_{2} \mathrm{a}_{11}-\mathrm{b}_{1} \mathrm{a}_{21}$

## Introducing determinant:

$$
\left.\begin{aligned}
& a_{11} \\
& a_{12} \\
& a_{21} \\
& a_{22}
\end{aligned}\left|=a_{11} a_{22}-a_{12} a_{21}, x_{1}=\left|\begin{array}{ll}
b_{1} & a_{12} \\
b_{2} & a_{22}
\end{array}\right|, \begin{array}{ll}
a_{11} & a_{12} \\
a_{21} & a_{22}
\end{array}\right| \begin{array}{ll}
a_{11} & b_{1} \\
a_{21} & b_{2}
\end{array} \right\rvert\,
$$

Our case: $\mathrm{b}_{1}=\mathrm{b}_{2}=0$, homogeneous

1. trivial solution: $x_{1}=x_{2}=0$
2. nontrivial solution:

$$
\left.\begin{array}{ll}
a_{11} & a_{12} \\
a_{21} & a_{22}
\end{array} \right\rvert\,=0
$$

## $n$ linear equations for $n$ unknown variables

$$
\begin{aligned}
& \mathrm{a}_{11} X_{1}+\mathrm{a}_{12} X_{2}+\ldots+\mathrm{a}_{1 \mathrm{n}} X_{\mathrm{n}}= \\
& \mathrm{b}_{1} \\
& \mathrm{a}_{21} X_{1}+\mathrm{a}_{22} X_{2}+\ldots+\mathrm{a}_{2 \mathrm{n}} X_{\mathrm{n}}= \\
& \mathrm{b}_{2}
\end{aligned}
$$

$\operatorname{zu}^{2} \quad{ }^{[4} 0$
.
${ }^{27}$ $2 I_{0} \quad I_{0}$
$=\left({ }^{(!)} \mathfrak{e}\right) \nmid ə \mathrm{p}$

## ‘Әләчм

> ${ }^{2 \mathrm{u}} 0 \quad{ }^{[\mathrm{U}} 0$
> ${ }^{2}$
> ${ }^{22} 0$
> $I_{0}$
> ${ }^{2} 10$
> ${ }^{[1}$ e

$$
\begin{aligned}
& { }^{\text {un }} \\
& { }^{I+y^{6} u} \mathcal{Q} \quad{ }^{z} q \\
& \text { I-y‘u } \\
& { }^{4}{ }^{2} \\
& 1+y^{\prime} \tau_{p} \quad{ }^{2} q \\
& { }^{I+}+{ }^{6}{ }^{2} \quad{ }^{\mathrm{I}} \mathrm{q} \\
& \text { [-Y‘ }
\end{aligned}
$$

## inhomogeneous case: $\mathrm{b}_{\mathrm{k}} \neq 0$ for at least one $k$

$\left|\begin{array}{cccccccc}a_{11} & a_{12} & \cdots & a_{1, k-1} & b_{1} & a_{1, k+1} & \cdots & a_{1 n} \\ a_{21} & a_{22} & \cdots & a_{2, k-1} & b_{2} & a_{2, k+1} & \cdots & a_{2 n} \\ \cdot & \cdot & \cdots & \cdot & \cdot & \cdot & \cdots & \cdot \\ a_{n 1} & a_{n 2} & \cdots & a_{n, k-1} & b_{2} & a_{n, k+1} & \cdots & a_{n n}\end{array}\right|$
$X_{\mathrm{k}}=$
$\operatorname{det}\left(\mathrm{a}_{\mathrm{ij}}\right)$

## homogeneous case: $\mathrm{b}_{\mathrm{k}}=0, k=1,2, \ldots, n$

## (a) travial case: $x_{\mathrm{k}}=0, k=1,2, \ldots, n$

(b) nontravial case: $\operatorname{det}\left(\mathrm{a}_{\mathrm{ij}}\right)=0$

For a n-th order determinant, $\operatorname{det}\left(\mathrm{a}_{\mathrm{ij}}\right)=\sum_{\mathrm{l}=1}^{\mathrm{n}} \mathrm{a}_{\mathrm{lk}} \mathrm{C}_{1 \mathrm{k}}$ where, $\mathrm{C}_{\mathrm{lk}}$ is called cofactor

Trial wave function $\phi$ is a variation function which is a combination of $n$ linear independent functions $\left\{f_{1}, f_{2}, \ldots f_{n}\right\}$,

$$
\phi=c_{1} f_{1}+c_{2} f_{2}+\ldots+c_{\mathrm{n}} f_{\mathrm{n}}
$$

$$
\begin{aligned}
& \Rightarrow \sum_{\mathrm{k}=1}^{\mathrm{n}}\left[\left(H_{\mathrm{ik}}-S_{\mathrm{ik}} W\right) c_{\mathrm{k}}\right]=0 \quad i=1,2, \ldots, n \\
& S_{\mathrm{ik}} \equiv \int d \tau f_{i} f_{k} \\
& H_{\mathrm{ik}} \equiv \int d \tau f_{i} H f_{k} \\
& W \equiv \int d \tau \phi H \phi / \int d \tau \phi \phi
\end{aligned}
$$

## Linear variational theorem

(i) $W_{1} \leq W_{2} \leq \ldots \leq W_{\mathrm{n}}$ are $n$ roots of Eq.(1),
(ii) $E_{1} \leq E_{2} \leq \ldots \leq E_{\mathrm{n}} \leq E_{\mathrm{n}+1} \leq \ldots$ are energies of eigenstates;
then, $W_{1} \geq E_{1}, W_{2} \geq E_{2}, \ldots, W_{\mathrm{n}} \geq E_{\mathrm{n}}$

## Molecular Orbital (MO):

$$
\begin{aligned}
& \phi=\mathrm{c}_{1} \psi_{1}+\mathrm{c}_{2} \psi_{2} \\
& \left(\mathrm{H}_{11}-\mathrm{W}\right) \mathrm{c}_{1}+\left(\mathrm{H}_{12}-\mathrm{SW}\right) \mathrm{c}_{2}=0 \\
& \mathrm{~S}_{11}=1 \\
& \left(\mathrm{H}_{21}-\mathrm{SW}\right) \mathrm{c}_{1}+\left(\mathrm{H}_{22}-\mathrm{W}\right) \mathrm{c}_{2}=0 \\
& \mathrm{~S}_{22}=1
\end{aligned}
$$

Generally : $\left\{\psi_{\mathrm{i}}\right\}$ a set of atomic orbitals, basis set LCAO-MO $\quad \phi=c_{1} \psi_{1}+c_{2} \psi_{2}+\ldots \ldots+c_{n} \phi_{n}$ linear combination of atomic orbitals

$$
\begin{aligned}
& \sum_{\mathrm{k}=1}^{\mathrm{n}}\left(\mathrm{H}_{\mathrm{ik}}-\mathrm{S}_{\mathrm{ik}} \mathrm{~W}\right) \mathrm{c}_{\mathrm{k}}=0 \quad \mathrm{i}=1,2, \ldots \ldots, \mathrm{n} \\
& H_{\mathrm{ik}} \equiv \int d \tau \psi_{i}^{*} H \psi_{k} \quad S_{\mathrm{ik}} \equiv \int d \tau \psi_{i}^{*} \psi_{k} \quad S_{k k}=1
\end{aligned}
$$

## The Born-Oppenheimer Approximation

## Hamiltonian

$$
\begin{aligned}
\boldsymbol{H}= & \sum_{\alpha}\left(-\mathbf{h}^{2} / 2 \mathbf{m}_{\alpha}\right) \nabla_{\alpha}^{2}-\left(\mathbf{h}^{2} / 2 \mathrm{~m}_{\mathrm{e}}\right) \sum_{\mathrm{i}} \nabla_{\mathrm{i}}^{2} \\
& +\sum_{\alpha} \sum_{\beta} \mathbf{Z}_{\alpha} \mathbf{Z}_{\beta} \mathbf{e}^{2} / \mathbf{r}_{\alpha \beta}-\sum_{\mathrm{i}} \sum_{\alpha} \mathbf{Z}_{\alpha} \mathbf{e}^{2} / \mathbf{r}_{\mathrm{i} \alpha} \\
& +\sum_{\mathrm{i}} \sum_{\mathrm{j}} \mathbf{e}^{2} / \mathbf{r}_{\mathrm{i}}{ }_{\mathrm{ij}}
\end{aligned}
$$

$$
H \psi\left(\mathbf{r}_{\mathrm{i}} ; \mathrm{r}_{\alpha}\right)=E \psi\left(\mathrm{r}_{\mathrm{i}} ; \mathrm{r}_{\alpha}\right)
$$

## The Born-Oppenheimer Approximation:

(1) $\psi\left(\mathbf{r}_{\mathrm{i}} ; \mathbf{r}_{\alpha}\right)=\psi_{\mathrm{el}}\left(\mathbf{r}_{\mathbf{i}} ; \mathbf{r}_{\alpha}\right) \psi_{\mathrm{N}}\left(\mathbf{r}_{\alpha}\right)$
(2) $H_{\mathrm{el}}\left(\mathbf{r}_{\alpha}\right)=-\left(\mathbf{h}^{2} / 2 \mathrm{~m}_{\mathrm{e}}\right) \sum_{\mathrm{i}} \nabla_{\mathrm{i}}^{2}-\sum_{\mathrm{i}} \Sigma_{\alpha} \mathrm{Z}_{\alpha} \mathbf{e}^{2} / \mathbf{r}_{\mathrm{i} \alpha}$ $+\sum_{\mathrm{i}} \Sigma_{\mathrm{j}} \mathbf{e}^{2} / \mathbf{r}_{\mathrm{ij}}$
$V_{\mathrm{NN}}=\sum_{\alpha} \Sigma_{\beta} \mathbf{Z}_{\alpha} \mathbf{Z}_{\beta} \mathbf{e}^{2} / \mathbf{r}_{\alpha \beta}$
$\boldsymbol{H}_{\mathrm{el}}\left(\mathbf{r}_{\alpha}\right) \psi_{\mathrm{el}}\left(\mathbf{r}_{\mathrm{i}} ; \mathbf{r}_{\alpha}\right)=E_{\mathrm{el}}\left(\mathbf{r}_{\alpha}\right) \psi_{\mathrm{el}}\left(\mathbf{r}_{\mathrm{i}} ; \mathbf{r}_{\alpha}\right)$
(3) $\boldsymbol{H}_{\mathrm{N}}=\Sigma_{\alpha}\left(-\mathbf{h}^{2} / 2 \mathrm{~m}_{\alpha}\right) \nabla_{\alpha}^{2}+\boldsymbol{U}\left(\mathbf{r}_{\alpha}\right)$
$\boldsymbol{U}\left(\mathbf{r}_{\alpha}\right)=E_{\mathrm{el}}\left(\mathbf{r}_{\alpha}\right)+\boldsymbol{V}_{\mathrm{NN}}$
$\boldsymbol{H}_{\mathrm{N}}\left(\mathrm{r}_{\alpha}\right) \psi_{\mathrm{N}}\left(\mathrm{r}_{\alpha}\right)=E \psi_{\mathrm{N}}\left(\mathrm{r}_{\alpha}\right)$

## Assignment <br> Calculate the ground state energy and bond length of $\mathrm{H}_{2}$ using the HyperChem with the $6-31 \mathrm{G}$ <br> (Hint: Born-Oppenheimer Approximation)

## Hydrogen Molecule $\mathbf{H}_{2}$

## e


+

## The Pauli principle

two electrons cannot be in the same state.

## Wave function:

$$
\begin{aligned}
& \phi(1,2)=\varphi_{a}(1) \varphi_{b}(2)+c_{1} \varphi_{a}(2) \varphi_{b}(1) \\
& \phi(2,1)=\varphi_{a}(2) \varphi_{b}(1)+c_{1} \varphi_{a}(1) \varphi_{b}(2)
\end{aligned}
$$

Since two wave functions that correspond to the same state can differ at most by a constant factor

$$
\begin{gathered}
\phi(1,2)=\mathbf{c}_{2} \phi(2,1) \\
\varphi_{\mathrm{a}}(1) \varphi_{\mathrm{b}}(2)+\mathrm{c}_{1} \varphi_{\mathrm{a}}(2) \varphi_{\mathrm{b}}(1)=\mathbf{c}_{2} \varphi_{\mathrm{a}}(2) \varphi_{\mathrm{b}}(1)+\mathrm{c}_{2} \mathrm{c}_{1} \varphi_{\mathrm{a}}(1) \varphi_{\mathrm{b}}(2) \\
\mathbf{c}_{1}=\mathbf{c}_{2} \quad \mathbf{c}_{2} \mathbf{c}_{1}=1
\end{gathered}
$$

Therefore: $c_{1}=c_{2}= \pm 1$
According to the Pauli principle, $\quad \mathrm{c}_{1}=\mathrm{c}_{2}=-1$

## The Pauli principle (different version)

the wave function of a system of electrons must be antisymmetric with respect to interchanging of any two electrons.

Wave function $\phi$ of $\mathrm{H}_{2}$ : Slater Determinant

$$
\psi(1,2)=1 / \sqrt{2}![\phi(1) \alpha(1) \phi(2) \beta(2)-\phi(2) \alpha(2) \phi(1) \beta(1)]
$$

$$
=1 / \sqrt{2}!\left\lvert\, \begin{array}{ll}
\phi(1) \alpha(1) & \phi(2) \alpha(2) \\
\phi(1) \beta(1) & \phi(2) \beta(2)
\end{array}\right.
$$

## Energy: $E_{\psi}$

$E_{\psi}=2 \int \mathrm{~d} \tau_{1} \phi^{*}(1)\left(T_{\mathrm{e}}+V_{\text {eN }}\right) \phi(1)+V_{\mathrm{NN}}$
$+\int \mathrm{d} \tau_{1} \mathrm{~d} \tau_{2}\left|\phi^{2}(1)\right| \mathrm{e}^{2} / \mathrm{r}_{12}\left|\phi^{2}(2)\right|$
$=\sum_{\mathrm{i}=1,2} f_{\mathrm{ii}}+J_{12}+V_{\mathrm{NN}}$
To minimize $\boldsymbol{E}_{\psi}$ under the constraint $. d \tau\left|\phi^{2}\right|=1$, use Lagrange's method:
$L=E \psi-2 \varepsilon\left[/ \mathrm{d} \tau_{1}\left|\phi^{2}(1)\right|-1\right]$
$\delta L=\delta E \psi-4 \varepsilon \int \mathrm{~d} \tau_{1} \phi^{*}(1) \delta \phi(1)$
$=4 \int \mathrm{~d} \tau_{1} \delta \phi^{*}(1)\left(T_{\mathrm{e}}+V_{\mathrm{eN}}\right) \phi(1)$
$+4 \int \mathrm{~d} \tau_{1} \mathrm{~d} \tau_{2} \phi^{*}(1) \phi^{*}(2) \mathrm{e}^{2} / \mathrm{r}_{12} \phi(2) \delta \phi(1)$ $-4 \varepsilon \int \mathrm{~d} \tau_{1} \phi^{*}(1) \delta \phi(1)$
$=0$

## $\left[T_{\mathrm{e}}+V_{\mathrm{eN}}+\int \mathrm{d} \tau_{2} \phi^{*}(2) \mathrm{e}^{2} / \mathrm{r}_{12} \phi(2)\right] \phi(1)=\varepsilon \phi(1)$

## Average Hamiltonian

## Hartree-Fock equation

$(f+J) \phi=\varepsilon \phi$
$R(1)=T_{\mathrm{e}}(1)+V_{\mathrm{eN}}(1) \quad$ one electron operator $J(1)=\int \mathrm{d} \tau_{2} \phi^{*}(2) \mathrm{e}^{2} / \mathrm{r}_{12} \phi(2) \quad$ two electron Coulomb operator
(1) is the Hamiltonian of electron $\mathbf{1}$ in the absence of electron 2 ;
$\boldsymbol{J}(\mathbf{1})$ is the mean Coulomb repulsion exerted on electron 1 by 2 ;
$\varepsilon$ is the energy of orbital $\phi$.

$$
\text { LCAO-MO: } \quad \phi=\mathrm{c}_{1} \psi_{1}+\mathrm{c}_{2} \psi_{2}
$$

Multiple $\psi_{1}$ from the left and then integrate :
$\mathrm{c}_{1} F_{11}+\mathrm{c}_{2} F_{12}=\varepsilon\left(\mathrm{c}_{1}+S \mathrm{c}_{2}\right)$

## Multiple $\psi_{2}$ from the left and then integrate :

$$
\mathrm{c}_{1} F_{12}+\mathrm{c}_{2} F_{22}=\varepsilon\left(S \mathrm{c}_{1}+\mathrm{c}_{2}\right)
$$

where,

$$
\begin{aligned}
& F_{\mathrm{ij}}=\int \mathrm{d} \tau \psi_{\mathrm{i}}^{*}(\boldsymbol{f}+\boldsymbol{J}) \psi_{\mathrm{j}}=H_{\mathrm{ij}}+\int \mathrm{d} \tau \psi_{\mathrm{i}}^{*} \boldsymbol{J} \psi_{\mathrm{j}} \\
& S^{=}=\int \mathrm{d} \tau \psi_{1} \psi_{2} \\
& \left(F_{11}-\varepsilon\right) \mathrm{c}_{1}+\left(F_{12}-S \varepsilon\right) \mathrm{c}_{2}=0 \\
& \left(F_{12}-S \varepsilon\right) \mathrm{c}_{1}+\left(F_{22}-\varepsilon\right) \mathrm{c}_{2}=0
\end{aligned}
$$

## Secular Equation:

$$
\left|\begin{array}{ll}
F_{11}-\varepsilon & F_{12}-S \varepsilon \\
F_{12}-S \varepsilon & F_{22}-\varepsilon
\end{array}\right|=0
$$

bonding orbital:

$$
\begin{aligned}
& \varepsilon_{1}=\left(\boldsymbol{F}_{11}+\boldsymbol{F}_{12}\right) /(\boldsymbol{1}+\boldsymbol{S}) \\
& \phi_{1}=\left(\psi_{1}+\psi_{2}\right) / \sqrt{ } 2(1+\boldsymbol{S})^{1 / 2}
\end{aligned}
$$

antibonding orbital: $\varepsilon_{2}=\left(F_{11}-F_{12}\right) /(1-S)$

$$
\phi_{2}=\left(\psi_{1}-\psi_{2}\right) / \sqrt{2}(1-S)^{1 / 2}
$$

## Molecular Orbital Configurations of Homo nuclear Diatomic Molecules $\mathbf{H}_{\mathbf{2}}, \mathrm{Li}_{\mathbf{2}}, \mathbf{O}, \mathbf{H e}_{2}$, etc

| Moecule | Bond order | De/eV |
| :---: | :---: | :---: |
| $\mathrm{H}_{2}{ }^{+}$ | - | 2.79 |
| $\mathrm{H}_{2}$ | 1 | 4.75 |
| $\mathrm{He}_{2}{ }^{+}$ | \% | 1.08 |
| $\mathrm{He}_{2}$ | 0 | 0.0009 |
| $\mathrm{Li}_{2}$ | 1 | 1.07 |
| $\mathrm{Be}_{2}$ | 0 | 0.10 |
| $\mathrm{C}_{2}$ | 2 | 6.3 |
| $\mathbf{N}_{2}{ }^{+}$ | - | 8.85 |
| $\mathrm{N}_{2}$ | 3 | 9.91 |
| $\mathrm{O}_{2}{ }^{+}$ | 2 | 6.78 |
| $\mathrm{O}_{2}$ | 2 | 5.21 |

The more the Bond Order is, the stronger the chemical bond is.




Bond Order: one-half the difference between the number of bonding and antibonding electrons

## $\phi_{1}$ $\phi_{2}$

$$
\begin{gathered}
\phi_{2}(1) \alpha(1) \\
\phi_{2}(2) \alpha(2) \\
\left.\phi_{2}(1) \phi_{1}(2)\right] \alpha(1) \alpha(2)
\end{gathered}
$$


$\square=\square-\infty=$

## $\psi(1,2)=1 / \sqrt{ } 2$ <br> $\phi_{1}(2) \alpha(2)$ <br> $=1 / \sqrt{2}\left[\phi_{1}(1) \phi_{2}(2)-\right.$

$$
\begin{aligned}
E_{\psi} & =\int \mathrm{d} \tau_{1} \mathrm{~d} \tau_{2} \psi^{*} H \psi \\
& =\int \mathrm{d} \tau_{1} \mathrm{~d} \tau_{2} \psi^{*}\left(T_{1}+V_{1 \mathrm{~N}}+T_{2}+V_{2 \mathrm{~N}}+V_{12}+V_{\mathrm{NN}}\right) \psi \\
& =<\phi_{1}(1)\left|T_{1}+V_{1 \mathrm{~N}}\right| \phi_{1}(1)> \\
& +<\phi_{2}(2)\left|T_{2}+V_{2 \mathrm{~N}}\right| \phi_{2}(2)> \\
& +<\phi_{1}(1) \phi_{2}(2)\left|V_{12}\right| \phi_{1}(1) \phi_{2}(2)> \\
& -<\phi_{1}(2) \phi_{2}(1)\left|V_{12}\right| \phi_{1}(1) \phi_{2}(2)>+V_{\mathrm{NN}} \\
& =\sum_{\mathrm{i}}<\phi_{i}(1)\left|T_{1}+V_{1 \mathrm{~N}}\right| \phi_{i}(1)> \\
& +<\phi_{1}(1) \phi_{2}(2)\left|V_{12}\right| \phi_{1}(1) \phi_{2}(2)> \\
& -<\phi_{1}(2) \phi_{2}(1)\left|V_{12}\right| \phi_{1}(1) \phi_{2}(2)>+V_{\mathrm{NN}} \\
& =\sum_{\mathrm{i}=1,2} f_{\mathrm{ii}}+J_{12}-K_{12}+V_{\mathrm{NN}}
\end{aligned}
$$

## - $K_{2}(1)$ - $\boldsymbol{K}_{1}(\mathbf{2})$

## $\sum_{\alpha} Z_{\alpha} / \mathbf{r}_{j \alpha}$

 $\mathrm{e}^{2} / \mathrm{r}_{12} \phi_{\mathrm{j}}(2)$) $\mathrm{e}^{2 / r_{12}} \theta(2)$

## Average Hamiltonian

Particle One: $\quad(1)+J_{2}(1)$ Particle Two: $1(2)+J_{1}(2)$

$$
f(\mathrm{j}) \equiv-\left(\mathrm{h}^{2} / 2 \mathrm{~m}_{\mathrm{e}}\right) \nabla_{\mathrm{j}}^{2}-
$$

$$
J_{j}(1) \theta(1) \equiv \theta(1) / \mathrm{dr}_{2} \phi_{\mathrm{j}}(2
$$

$$
K_{\mathrm{j}}(1) \theta(1) \equiv \phi_{\mathrm{j}}(1) / \mathrm{dr}_{2} \phi_{\mathrm{j}}^{*}(2
$$

## Hartree-Fock Equation:

$$
\begin{aligned}
& \left.[\boldsymbol{f} \mathbf{1})+\boldsymbol{J}_{\mathbf{2}}(\mathbf{1})-\boldsymbol{K}_{\mathbf{2}}(\mathbf{1})\right] \phi_{1}(1)=\varepsilon_{1} \phi_{1}(1) \\
& {\left[\boldsymbol{f} \mathbf{( 2 )}+\boldsymbol{J}_{\mathbf{1}}(\mathbf{2})-\boldsymbol{K}_{\mathbf{1}}(\mathbf{2})\right] \phi_{2}(2)=\varepsilon_{2} \phi_{2}(2)}
\end{aligned}
$$

## Fock Operator:

$\mathbf{F}(\mathbf{1}) \equiv \boldsymbol{1}(\mathbf{1})+J_{\mathbf{2}}(\mathbf{1})-K_{\mathbf{2}}(\mathbf{1})$ Fock operator for 1
$\mathbf{F}(\mathbf{2}) \equiv \boldsymbol{f} \mathbf{( 2 )}+\boldsymbol{J}_{\mathbf{1}} \mathbf{( 2 )}-\boldsymbol{K}_{\mathbf{1}}(\mathbf{2})$ Fock operator for 2

## Hartree-Fock Method

1. Many-Body Wave Function is approximated by Slater Determinant
2. Hartree-Fock Equation
$\boldsymbol{F} \phi_{\mathrm{i}}=\varepsilon_{\mathrm{i}} \phi_{\mathrm{i}}$
$\boldsymbol{F}$ Fock operator
$\phi_{i}$ the $i$-th Hartree-Fock orbital
$\varepsilon_{\mathrm{i}}$ the energy of the $i$-th Hartree-Fock orbital
3. Roothaan Method (introduction of Basis functions) $\phi_{\mathrm{i}}=\sum_{\mathrm{k}} \mathrm{c}_{\mathrm{ki}} \psi_{\mathrm{k}}$ LCAO-MO
$\left\{\psi_{\mathrm{k}}\right\}$ is a set of atomic orbitals (or basis functions)
4. Hartree-Fock-Roothaan equation $\Sigma_{\mathrm{j}}\left(F_{\mathrm{ij}}-\varepsilon_{\mathrm{i}} \boldsymbol{S}_{\mathrm{ij}}\right) \boldsymbol{c}_{\mathrm{ij}}=\mathbf{0}$

$$
\boldsymbol{F}_{\mathrm{ij}} \equiv\left\langle\psi_{\mathrm{i}}\right| \boldsymbol{F}\left|\psi_{\mathrm{j}}\right\rangle \quad \boldsymbol{S}_{\mathrm{ij}} \equiv\left\langle\psi_{\mathrm{i}} \mid \psi_{\mathrm{j}}\right\rangle
$$

5. Solve the Hartree-Fock-Roothaan equation self-consistently

## , 10.8,

Assignment one

$$
\begin{aligned}
& 8.40,10.5,10.6,10.7 \\
& 11.37,13.37
\end{aligned}
$$

## Summary

1. At the Hartree-Fock Level there are two possible Coulomb integrals contributing the energy between two electrons $\boldsymbol{i}$ and $\boldsymbol{j}$ : Coulomb integrals $\boldsymbol{J}_{\mathrm{ij}}$ and exchange integral $\boldsymbol{K}_{\mathrm{ij}}$;
2. For two electrons with different spins, there is only Coulomb integral $J_{\mathrm{ij}}$;
3. For two electrons with the same spins, both Coulomb and exchange integrals exist.
4. Total Hartree-Fock energy consists of the contributions from one-electron integrals $\boldsymbol{f}_{\mathrm{ii}}$ and two-electron Coulomb integrals $\boldsymbol{J}_{\mathrm{ij}}$ and exchange integrals $\boldsymbol{K}_{\mathrm{ij}}$;
5. At the Hartree-Fock Level there are two possible Coulomb potentials (or operators) between two electrons $\boldsymbol{i}$ and $\boldsymbol{j}$ : Coulomb operator and exchange operator; $\boldsymbol{J}_{\mathbf{j}} \mathbf{i} \mathbf{i}$ is the Coulomb potential (operator) that $\boldsymbol{i}$ feels from $\boldsymbol{j}$, and $\boldsymbol{K}_{\mathbf{j}} \mathbf{i}$ ) is the exchange potential (operator) that that $\boldsymbol{i}$ feels from $\boldsymbol{j}$.
6. Fork operator (or, average Hamiltonian) consists of one-electron operators $\boldsymbol{f} \mathbf{( i )}$ and Coulomb operators $\boldsymbol{J}_{\mathbf{j}}(\mathbf{i})$ and exchange operators $\boldsymbol{K}_{\mathbf{j}}(\mathbf{i})$

$\boldsymbol{N}_{\alpha}$ electrons spin up and $\boldsymbol{N}_{\beta}$ electrons spin down.
Fock matrix for an electron $\mathbf{1}_{\alpha}$ with spin up:

$$
\begin{array}{r}
\boldsymbol{F}^{\alpha}\left(\mathbf{1}_{\alpha}\right)=\boldsymbol{f}^{\alpha}\left(\mathbf{1}_{\alpha}\right)+\sum_{\mathrm{j}}\left[\boldsymbol{J}_{\mathrm{j}}^{\alpha}\left(\mathbf{1}_{\alpha}\right)-\boldsymbol{K}_{\mathrm{j}}^{\alpha}\left(\mathbf{1}_{\alpha}\right)\right]+\sum_{\mathrm{j}} \boldsymbol{J}_{\mathrm{j}}^{\mathrm{B}}\left(\mathbf{1}_{\alpha}\right) \\
\mathrm{j}=1_{\alpha}, N \alpha \\
\mathrm{j}=1_{\beta}, N_{\beta}
\end{array}
$$

Fock matrix for an electron $1_{\beta}$ with spin down:

$$
\begin{aligned}
& \boldsymbol{F}^{\beta}\left(\mathbf{1}_{\beta}\right)=\boldsymbol{f}^{\boldsymbol{\beta}}\left(\mathbf{1}_{\beta}\right)+\sum_{\mathrm{j}}\left[\boldsymbol{J}_{\mathrm{j}}{ }^{\beta}\left(\mathbf{1}_{\beta}\right)-\boldsymbol{K}_{\mathrm{j}}^{\boldsymbol{\beta}}\left(\mathbf{1}_{\beta}\right)\right]+\sum_{\mathrm{j}} \boldsymbol{J}_{\mathrm{j}}^{\alpha}\left(\mathbf{1}_{\beta}\right) \\
& \mathrm{j}=1_{\beta}, N_{\beta} \\
& \mathrm{j}=1_{\alpha} N_{\alpha}
\end{aligned}
$$

$$
\begin{aligned}
& f(1) \equiv-\left(h^{2} / 2 \mathrm{~m}_{\mathrm{e}}\right) \nabla_{1}{ }^{2}-\sum_{\mathrm{N}} \mathrm{Z}_{\mathrm{N}} / \mathbf{r}_{1 \mathrm{~N}} \\
& J_{\mathrm{j}}^{\alpha}(1) \equiv \int \mathrm{dr}_{2} \phi_{\mathrm{j}}^{\alpha{ }^{\alpha}}(2) \mathrm{e}^{2} / \mathbf{r}_{12} \phi_{\mathrm{j}}^{\alpha}(2) \\
& K_{\mathrm{j}}^{\alpha}(1) \theta(1) \equiv \phi_{\mathrm{j}}^{\alpha}(1) / \mathrm{dr}_{2} \phi_{\mathrm{j}}^{\alpha^{*}}(2) \mathrm{e}^{2} / \mathbf{r}_{12} \theta(2)
\end{aligned}
$$

Energy $=\sum_{\mathrm{j}}^{\alpha} \boldsymbol{f}_{j j}^{\alpha}+\sum_{\mathrm{j}}{ }^{\beta} \boldsymbol{f}_{j j}{ }^{\beta}+(\mathbf{1} / \mathbf{2}) \sum_{\mathrm{i}}{ }^{\alpha} \sum_{\mathrm{j}}{ }^{\alpha}\left(J_{\mathrm{ij}}{ }^{\alpha \alpha}-\boldsymbol{K}_{\mathrm{ij}}{ }^{\alpha \alpha}\right)$ $+(\mathbf{1} / \mathbf{2}) \sum_{\mathrm{i}}^{\alpha} \sum_{\mathrm{j}}{ }^{\beta}\left(J_{\mathrm{ij}}{ }^{\beta \beta}-\boldsymbol{K}_{\mathrm{ij}}{ }^{\beta \beta}\right)+\sum_{\mathrm{i}}^{\alpha} \sum_{\mathrm{j}}{ }^{\beta}{ }_{\boldsymbol{J}_{\mathrm{ij}}{ }^{\alpha \beta}}$
$\therefore V_{\mathrm{NN}}$

$$
\mathrm{i}=1, N_{\alpha} \mathrm{j}=1, N_{\beta}
$$

$$
\begin{aligned}
& f_{\mathrm{ij}} \equiv f_{\mathrm{ij}}^{\alpha} \equiv\left\langle\phi_{\mathrm{j}}{ }^{\alpha}\right| \boldsymbol{f}\left|\phi_{\mathrm{j}}^{\alpha}\right\rangle \\
& J_{\mathrm{ij}} \equiv J_{\mathrm{ij}}{ }^{\alpha \alpha} \equiv\left\langle\phi^{\alpha}{ }_{\mathrm{j}}(2)\right| J_{\mathrm{i}}{ }^{\alpha}(1)\left|\phi^{\alpha}{ }_{\mathrm{j}}(2)\right\rangle \\
& K_{\mathrm{ij}} \equiv K_{\mathrm{ij}}{ }^{\alpha \alpha} \equiv\left\langle\phi^{\alpha}{ }_{\mathrm{j}}(2)\right| K_{\mathrm{i}}^{\alpha}(1) \mid \phi^{\alpha}{ }_{\mathrm{j}}(2)> \\
& J_{\mathrm{ij}} \equiv J_{\mathrm{ij}}{ }^{\alpha} \beta \equiv\left\langle\phi^{\beta}{ }_{\mathrm{j}}{ }^{(2)}\right| J_{\mathrm{i}}{ }^{\alpha}(1)\left|\phi_{\mathrm{j}}{ }_{\mathrm{j}}(2)\right\rangle
\end{aligned}
$$

Close subshell case: $\left(N_{\alpha}=N_{\beta}=\mathbf{n} / 2\right)$
$F(\mathbf{1})=f(\mathbf{1})+\sum_{\mathrm{j}=1, \mathrm{n} / 2}\left[\mathbf{2} J_{\mathrm{j}}(\mathbf{1})-K_{\mathrm{j}}(\mathbf{1})\right]$
Energy $=2 \sum_{\mathrm{j}=1, \mathrm{n} / 2} f_{j j}+\sum_{\mathrm{i}=1, \mathrm{n} / 2} \Sigma_{\mathrm{j}=1, \mathrm{n} / 2}\left(2 J_{\mathrm{ij}}-K_{\mathrm{ij}}\right)+V_{\mathrm{NN}}$

## The Condon-Slater Rules

$<\phi_{a}(1) \phi_{b}(2) \phi_{c}(3) \ldots \phi_{d}(\mathbf{n})|f(1)| \phi_{e}(1) \phi_{f}(2) \phi_{g}(3) \ldots \phi_{h}(\mathbf{n})>$
$=\left\langle\phi_{a}(1)\right| f(1)\left|\phi_{e}(1)\right\rangle\left\langle\phi_{b}(2) \phi_{c}(3) \ldots \phi_{d}(n)\right| \phi_{f}(2) \phi_{g}(3) \ldots \phi_{h}(n)>$
$\left.=<\phi_{\mathrm{a}}(1)|f(1)| \phi_{\mathrm{e}}(1)\right\rangle$

$$
\text { if } b=f, c=g, \ldots, d=h ; \quad 0 \text {, otherwise }
$$

$<\phi_{\mathrm{a}}(1) \phi_{\mathrm{b}}(2) \phi_{\mathrm{c}}(3) \ldots \phi_{\mathrm{d}}(\mathrm{n})\left|V_{12}\right| \phi_{\mathrm{e}}(1) \phi_{\mathrm{f}}(2) \phi_{\mathrm{g}}(3) \ldots \phi_{\mathrm{h}}(\mathbf{n})>$
$=<\phi_{\mathrm{a}}(1) \phi_{\mathrm{b}}(2)\left|V_{12}\right| \phi_{\mathrm{e}}(1) \phi_{\mathrm{f}}(2)><\phi_{\mathrm{c}}(3) \ldots \phi_{\mathrm{d}}(\mathrm{n}) \mid \phi_{\mathrm{g}}(3) \ldots \phi_{\mathrm{h}}(\mathrm{n})>$
$=\left\langle\phi_{\mathrm{a}}(1) \phi_{\mathrm{b}}(2)\right| V_{12}\left|\phi_{\mathrm{e}}(1) \phi_{\mathrm{f}}(2)\right\rangle$

## if $c=g, \ldots, d=h ; \quad 0$, otherwise

## LUMO

the lowest unoccupied molecular orbital $\Rightarrow$

## HOMO

the highest occupied molecular orbital


## Koopman's Theorem

The energy required to remove an electron from a closed-shell atom or molecules is well approximated by minus the orbital energy $\varepsilon$ of the AO or MO from which the electron is removed.

## Route section

Title

Molecule Specification (in Cartesian coordinates

## \# HF/6-31G(d)

## water energy

> | $\mathbf{0}$ |  |  |  |
| :--- | ---: | ---: | ---: |
| O | $-\mathbf{0 . 4 6 4}$ | 0.177 | 0.0 |
| H | $-\mathbf{0 . 4 6 4}$ | $\mathbf{1 . 1 3 7}$ | $\mathbf{0 . 0}$ |
| H | $\mathbf{0 . 4 4 1}$ | $-\mathbf{0 . 1 4 3}$ | $\mathbf{0 . 0}$ |

Basis Set $\phi_{i}=\sum_{p} c_{i p}$
mb


$$
\mathrm{ml}_{\mathrm{nlm}}=N r^{\mathrm{n}-1} \exp \left(-\xi r / a_{0}\right) Y_{\mathrm{lm}}(\theta, \phi)
$$

$\xi$ the orbital exponent

Gaussian type functions
$g_{\mathrm{ijk}}=N x^{\mathrm{i}} y^{\mathrm{j}} z^{\mathrm{k}} \exp \left(-\alpha r^{2}\right)$
(primitive Gaussian function)
$\mathrm{ml}_{\mathrm{p}}=\sum_{\mathrm{u}} d_{\mathrm{up}} g_{\mathrm{u}}$
(contracted Gaussian-type function, CGTF)
$\mathrm{u}=\{\mathrm{ijk}\} \quad \mathrm{p}=\{\mathrm{nlm}\}$

## Basis set of GTFs

STO-3G, 3-21G, 4-31G, 6-31G, 6-31G*, 6-31G**
complexity \& accuracy
Minimal basis set: one STO for each atomic orbital (AO)

STO-3G: 3 GTFs for each atomic orbital
3-21G: 3 GTFs for each inner shell AO
2 CGTFs (w/ 2 \& 1 GTFs) for each valence AO
6-31G: 6 GTFs for each inner shell AO
2 CGTFs (w/ $3 \& 1$ GTFs) for each valence AO
$6-31 \mathrm{G}^{*}$ : adds a set of d orbitals to atoms in $2 \mathrm{nd} \& 3$ rd rows $6-31 \mathrm{G}^{* *}$ : adds a set of d orbitals to atoms in $2 \mathrm{nd} \& 3$ rd rows and a set of $p$ functions to hydrogen

## Diffuse Basis Sets:

For excited states and in anions where electronic density is more spread out, additional basis functions are needed.

## Diffuse functions to 6-31G basis set as follows:

$6-31 G^{*}$ - adds a set of diffuse $s \& p$ orbitals to atoms in 1 st $\& 2$ nd rows ( $\mathrm{Li}-\mathrm{Cl}$ ).
$6-31 G^{* *}$ - adds a set of diffuse $s$ and $p$ orbitals to atoms in 1 st $\& 2$ nd rows $(\mathrm{Li}-\mathrm{Cl})$ and a set of diffuse s functions to H

Diffuse functions + polarisation functions:
$6-31+\mathrm{G}^{*}, 6-31++\mathrm{G}^{*}, 6-31+\mathrm{G}^{* *}$ and $6-31++\mathrm{G}^{* *}$ basis sets.

Double-zeta (DZ) basis set:
two STO for each AO

## $(10 \mathrm{~s} 4 \mathrm{p}) \rightarrow[3 \mathrm{~s} 2 \mathrm{p}]$



## 6-31G for a carbon atom:



Minimal basis set:

One STO for each inner-shell and valence-shell AO of each atom

## example: $\mathrm{C}_{2} \mathrm{H}_{2}(2 \mathrm{~S} 1 \mathrm{P} / 1 \mathrm{~S})$

C: 1S, 2S, 2P $\mathrm{P}_{\mathrm{x}}, \mathbf{2 P _ { y }}, 2 \mathrm{P}_{\mathrm{z}}$
H: 1S
total 12 STOs as Basis set

Double-Zeta (DZ) basis set:

> two STOs for each and $$
\text { valence-shell AO of each atom }
$$

example: $\mathrm{C}_{2} \mathrm{H}_{2}(4 \mathrm{~S} 2 \mathrm{P} / 2 \mathrm{~S})$
C: two 1S, two 2S, two $2 P_{x}$, two $2 P_{y}$, two $2 P_{z}$
H: two 1S (STOs)
total 24 STOs as Basis set

## Split -Valence (SV) basis set

Two STOs for each inner-shell and valence-shell AO One STO for each inner-shell AO

Double-zeta plus polarization set(DZ + P, or DZP)
Additional STO w/l quantum number larger than the $I_{\text {max }}$ of the valence - shell

* ( $\left.\mathbf{2 P}_{x}, 2 \mathrm{P}_{\mathrm{y}}, \mathbf{2 \mathrm { P } _ { \mathrm { z } }}\right)$ to H
* Five 3d Aos to Li-Ne, Na-Ar
* $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OSiH}_{3}$ :
(6s4p1d/4s2p1d/2s1p)



## Assignment two: Calculate the structure, ground

 state energy, molecular orbital energies, and vibrational modes and frequencies of a water molecule using Hartree-Fock method with 3-21G basis set.
## Ab Initio Molecular Orbital Calculation: $\mathbf{H}_{\mathbf{2}} \mathrm{O}$ (using HyperChem)

1. L-Click on (click on left button of Mouse) "Startup", and select and L-Click on "Program/Hyperchem".
2. Select "Build" and turn on "Explicit Hydrogens".
3. Select "Display" and make sure that "Show Hydrogens" is on; L-Click on "Rendering" and double L-Click "Spheres".
4. Double L-Click on "Draw" tool box and double L-Click on "O".
5. Move the cursor to the workspace, and L-Click \& release.
6. L-Click on "Magnify/Shrink" tool box, move the cursor to the workspace; L-press and move the cursor inward to reduce the size of oxygen atom.
7. Double L-Click on "Draw" tool box, and double L-Click on "H"; Move the cursor close to oxygen atom and L-Click \& release. A hydrogen atom appears. Draw second hydrogen atom using the same procedure.
8. L-Click on "Setup" \& select "Ab Initio"; double L-Click on 3-21G; then L-Click on "Option", select "UHF", and set "Charge" to 0 and "Multiplicity" to 1.
9. L-Click "Compute", and select "Geometry Optimization", and L-Click on "OK"; repeat the step till "Conv=YES" appears in the bottom bar. Record the energy.
10.L-Click "Compute" and L-Click "Orbitals"; select a energy level, record the energy of each molecular orbitals (MO), and L-Click "OK" to observe the contour plots of the orbitals.
11.L-Click "Compute" and select "Vibrations".
12.Make sure that "Rendering/Sphere" is on; L-Click "Compute" and select "Vibrational Spectrum". Note that frequencies of different vibrational modes.
13.Turn on "Animate vibrations", select one of the three modes, and L-Click "OK". Water molecule begins to vibrate. To suspend the animation, L-Click on "Cancel".

## The Hartree-Fock treatment of $\mathrm{H}_{2}$



## The Valence-Bond Treatment of $\mathrm{H}_{2}$

$$
\begin{aligned}
& \mathrm{f}_{1}=\psi_{1}(1) \psi_{2}(2) \\
& \mathrm{f}_{2}=\psi_{1}(2) \psi_{2}(1) \\
& \phi=\mathrm{c}_{1} \mathrm{f}_{1}+\mathrm{c}_{2} \mathrm{f}_{2} \\
& \underline{H}_{11}-\mathrm{W} \quad \underline{H}_{12}-\underline{S} \mathrm{~W} \mid=0 \\
& \underline{H}_{21}-\underline{S} \mathrm{~W} \quad \underline{H}_{22}-\mathrm{W} \mid \\
& \underline{H}_{11}=\underline{H}_{22}=<\psi_{1}(1) \psi_{2}(2)|H| \psi_{1}(1) \psi_{2}(2)> \\
& \underline{H}=\underline{H}_{21}=<\psi_{1}(1) \psi_{2}(2)|H| \psi_{1}(2) \psi_{2}(1)> \\
& \underline{S}=<\psi_{1}(1) \psi_{2}(2) \mid \psi_{1}(2) \psi_{2}(1)>\left[=S^{2}\right]
\end{aligned}
$$

The Heitler-London ground-state wave function $\left\{\left[\psi_{1}(1) \psi_{2}(2)+\psi_{1}(2) \psi_{2}(1)\right] / \sqrt{2}(1+\underline{S})^{1 / 2}\right\}[\alpha(1) \beta(2)-\alpha(2) \beta(1)] / \sqrt{2}$

## Comparison of the HF and VB Treatments

HF LCAO-MO wave function for $\mathrm{H}_{2}$

$$
\begin{aligned}
& {\left[\psi_{1}(1)+\psi_{2}(1)\right]\left[\psi_{1}(2)+\psi_{2}(2)\right]} \\
& =\psi_{1}(1) \psi_{1}(2)+\psi_{1}(1) \psi_{2}(2)+\psi_{2}(1) \psi_{1}(2)+\psi_{2}(1) \psi_{2}(2) \\
& \mathrm{H}^{-} \mathrm{H}^{+} \quad \mathrm{H}
\end{aligned} \mathrm{H} \quad \mathrm{H} \quad \mathrm{H} \quad \mathrm{H}^{+} \mathrm{H}^{-}-2 .
$$

VB wave function for $\mathrm{H}_{2}$

$$
\begin{array}{cccc}
\psi_{1}(1) & \psi_{2}(2)+\psi_{2}(1) & \psi_{1}(2) \\
H & \mathrm{H} & \mathrm{H} & \mathrm{H}
\end{array}
$$

At large distance, the system becomes

## H ............ H

MO: 50\% H ............ H $50 \% \quad \mathrm{H}^{+} . . . . . . . . . . . \mathrm{H}^{-}$
VB: 100\% H ............ H

The VB is computationally expensive and requires chemical intuition in implementation.

The Generalized valence-bond (GVB) method is a variational method, and thus computationally feasible. (William A. Goddard III)


The Valence-Bond Treatment of $\mathrm{H}_{2}$
$\left|\begin{array}{ll}H_{11}-W & H_{12}-S W \\ H_{21}-S W & H_{22}-W\end{array}\right|=0$

$$
\begin{aligned}
& f_{1}=\psi(1) \psi(2) \\
& f_{2}=\psi(2) \psi(1)
\end{aligned} \quad \Phi=c_{1} f_{1}+c_{2} f_{2}
$$



$$
\begin{aligned}
& H_{11}=H_{22}=\left\langle\psi_{1}(1) \psi_{2}(2)\right| H\left|\psi_{1}(1) \psi_{2}(2)\right\rangle \\
& H_{12}=H_{21}=\left\langle\psi_{1}(1) \psi_{2}(2)\right| H\left|\psi_{1}(2) \psi_{2}(1)\right\rangle \\
& S=\left\langle\psi_{1}(1) \psi_{2}(2) \mid \psi_{1}(2) \psi_{2}(1)\right\rangle\left[=S^{2}\right]
\end{aligned}
$$

The Heitler-London ground-state wave function

$$
\left\{\left[\psi_{1}(1) \psi_{2}(2)+\psi_{1}(2) \psi_{2}(1)\right] / \sqrt{2(1+S)}\right\}[\alpha(1) \beta(2)-\alpha(2) \beta(1)] / \sqrt{2}
$$

## Electron Correlation



## Electron Correlation: avoiding each other

Two reasons of the instantaneous correlation:
(1) Pauli Exclusion Principle (HF includes the effect)
(2) Coulomb repulsion (not included in the HF)

Beyond the Hartree-Fock
Configuration Interaction (CI)*
Perturbation theory*
Coupled Cluster Method
Density functional theory


$$
\begin{aligned}
& H^{0}=H_{1}{ }^{0}+H_{2}{ }^{0} \\
& \psi^{(0)}(1,2)=\mathrm{F}_{1}(1) \mathrm{F}_{2}(2) \\
& H_{1}^{0} \mathrm{~F}_{1}(1)=E_{1} \mathrm{~F}_{1}(1) \\
& H_{2}{ }^{0} \mathrm{~F}_{2}(1)=E_{2} \mathrm{~F}_{2}(1) \\
& E_{1}=-2 e^{2} / n_{1}{ }^{2} a_{0} \quad n_{1}=1,2,3, \ldots \\
& E_{2}=-2 e^{2} / n_{2}{ }^{2} a_{0} \quad n_{2}=1,2,3, \ldots
\end{aligned}
$$

## Ground state wave function

$$
\begin{aligned}
\psi^{(0)}(1,2) & =\left(1 \pi^{1 / 2}\right)\left(2 / a_{0} 3 / 2 \exp \left(-2 r_{i} / a_{0}\right) *\left(1 / \pi^{1 / 2}\right)\left(2 / a_{0}\right)^{3 / 2} \exp \left(-2 r_{l} / a_{0}\right)\right. \\
E^{(0)} & =-4 e^{2} / a_{0}
\end{aligned}
$$

$E^{(1)}=\left\langle\psi^{(0)}(1,2)\right| H^{\prime} \mid \psi^{(0)}(1,2)>=5 e^{2} / 4 a_{0}$ $E \approx E^{(0)}+E^{(1)}=-108.8+34.0=-74.8(\mathrm{eV})$ [compared with exp. -79.0 eV ]

## Nondegenerate Perturbation Theory (for Non-Degenerate Energy Levels)

$$
\begin{aligned}
& H=H^{0}+H^{\prime} \\
& H^{0} \Psi_{\mathrm{n}}^{(0)}=E_{\mathrm{n}}^{(0)} \Psi_{\mathrm{n}}{ }^{(0)}
\end{aligned}
$$

$\psi_{n}{ }^{(0)}$ is an eigenstate for unperturbed system $H^{\prime}$ is small compared with $H^{0}$

## Introducing a parameter $\lambda$

$$
\begin{aligned}
& H(\lambda)=H^{0}+\lambda H^{\prime} \\
& H(\lambda) \psi_{\mathrm{n}}(\lambda)=E_{\mathrm{n}}(\lambda) \psi_{\mathrm{n}}(\lambda) \\
& \psi_{\mathrm{n}}(\lambda)=\psi_{\mathrm{n}}^{(0)}+\lambda \psi_{\mathrm{n}}^{(1)}+\lambda^{2} \psi_{\mathrm{n}}^{(2)}+\ldots+\lambda^{k} \psi_{\mathrm{n}}^{(k)}+\ldots \\
& E_{\mathrm{n}}(\lambda)=E_{\mathrm{n}}^{(0)}+\lambda E_{\mathrm{n}}^{(1)}+\lambda^{2} E_{n}^{(2)}+\ldots+\lambda^{k} E_{n}^{(k)}+\ldots
\end{aligned}
$$

## $\lambda=1$, the original Hamiltonian

$$
\begin{aligned}
& \psi_{\mathrm{n}}=\psi_{\mathrm{n}}^{(0)}+\psi_{\mathrm{n}}^{(1)}+\psi_{\mathrm{n}}^{(2)}+\ldots+\psi_{\mathrm{n}}^{(k)}+\ldots \\
& E_{\mathrm{n}}=E_{\mathrm{n}}^{(0)}+E_{\mathrm{n}}^{(1)}+E_{\mathrm{n}}^{(2)}+\ldots+E_{\mathrm{n}}^{(\mathrm{k})}+\ldots
\end{aligned}
$$

Where, $\left\langle\psi_{\mathrm{n}}{ }^{(0)} \mid \psi_{\mathrm{n}}{ }^{(\mathrm{j})}\right\rangle=0, \mathrm{j}=1,2, \ldots, \mathrm{k}, \ldots$

## $H^{0} \psi_{\mathrm{n}}{ }^{(0)}=E_{\mathrm{n}}{ }^{(0)} \psi_{\mathrm{n}}{ }^{(0)}$ <br> $\Rightarrow$ solving for $E_{\mathrm{n}}{ }^{(0)}, \psi_{\mathrm{n}}{ }^{(0)}$

## $H^{0} \psi_{\mathrm{n}}{ }^{(1)}+H^{\prime} \psi_{\mathrm{n}}{ }^{(0)}=E_{\mathrm{n}}{ }^{(0)} \psi_{\mathrm{n}}{ }^{(1)}+E_{\mathrm{n}}{ }^{(1)} \psi_{\mathrm{n}}{ }^{(0)}$ $\Rightarrow$ olving for $E_{\mathrm{n}}{ }^{(1)}, \psi_{\mathrm{n}}{ }^{(1)}$

$$
\begin{aligned}
& H^{0} \psi_{\mathrm{n}}^{(2)}+H^{\prime} \psi_{\mathrm{n}}^{(1)}=E_{\mathrm{n}}^{(0)} \psi_{\mathrm{n}}^{(2)}+E_{\mathrm{n}}^{(1)} \psi_{\mathrm{n}}^{(1)}+E_{\mathrm{n}}^{(2)} \psi_{\mathrm{n}}{ }^{(0)} \\
& \Rightarrow \text { solving for } E_{\mathrm{n}}^{(2)}, \psi_{\mathrm{n}}^{(2)}
\end{aligned}
$$

## The first order:

Multiplied $\psi_{\mathrm{m}}{ }^{(0)}$ from the left and integrate,

$$
<\psi_{\mathrm{m}}^{(0)}\left|H^{0}\right| \psi_{\mathrm{n}}^{(1)}>+<\psi_{\mathrm{m}}^{(0)}\left|H^{\prime}\right| \psi_{\mathrm{n}}^{(0)}>=<\psi_{\mathrm{m}}^{(0)} \mid \psi_{\mathrm{n}}^{(1)}>E_{\mathrm{n}}^{(0)}+E_{\mathrm{n}}^{(1)} \delta_{\mathrm{mn}}
$$

$$
<\psi_{\mathrm{m}}^{(0)}\left|\psi_{\mathrm{n}}^{(1)}>\left[E_{\mathrm{m}}^{(0)}-E_{\mathrm{n}}^{(0)}\right]+<\psi_{\mathrm{m}}^{(0)}\right| H^{\prime} \mid \psi_{\mathrm{n}}^{(0)}>=E_{\mathrm{n}}^{(1)} \delta_{\mathrm{mn}}
$$

## For $\mathrm{m}=\mathrm{n}, \quad \boldsymbol{E}_{\mathrm{n}}{ }^{(1)}=\left\langle\psi_{\mathrm{n}}{ }^{(0)}\right| \boldsymbol{H}^{\prime}\left|\psi_{\mathrm{n}}{ }^{(0)}\right\rangle$ Eq. (1)

For $\mathrm{m} \neq \mathrm{n},\left\langle\psi_{\mathrm{m}}{ }^{(0)} \mid \psi_{\mathrm{n}}{ }^{(1)}\right\rangle=<\psi_{\mathrm{m}}{ }^{(0)}\left|H^{\prime}\right| \psi_{\mathrm{n}}{ }^{(0)}>/\left[E_{\mathrm{n}}{ }^{(0)}-E_{\mathrm{m}}{ }^{(0)}\right]$ If we expand $\psi_{\mathrm{n}}{ }^{(1)}=\sum \mathrm{c}_{\mathrm{nm}} \psi_{\mathrm{m}}{ }^{(0)}$,
$\mathrm{c}_{\mathrm{nm}}=<\psi_{\mathrm{m}}{ }^{(0)}\left|H^{\prime}\right| \psi_{\mathrm{n}}{ }^{(0)}>/\left[E_{\mathrm{n}}{ }^{(0)}-E_{\mathrm{m}}{ }^{(0)}\right]$ for $\mathrm{m} \neq \mathrm{n}$;
$\psi_{\mathrm{n}}{ }^{(1)}=\sum_{\mathrm{m}}<\psi_{\mathrm{m}}{ }^{(0)}\left|\boldsymbol{H}^{\prime}\right| \psi_{\mathrm{n}}{ }^{(0)}>/\left[\boldsymbol{E}_{\mathrm{n}}^{(0)}-\boldsymbol{E}_{\mathrm{m}}{ }^{(0)}\right] \psi_{\mathrm{m}}{ }^{(0)} \quad$ Eq.(2)

## The second order:

$$
\begin{aligned}
& <\psi_{\mathrm{m}}{ }^{(0)}\left|H^{\rho}\right| \psi_{\mathrm{n}}^{(2)}>+<\psi_{\mathrm{m}}^{(0)}|H| \psi_{\mathrm{n}}^{(1)}>=<\psi_{\mathrm{m}}^{(0)} \mid \psi_{\mathrm{n}}^{(2)} \\
& >E_{\mathrm{n}}^{(0)}+<\psi_{\mathrm{m}}^{(0)} \mid \psi_{\mathrm{n}}^{(1)}>E_{\mathrm{n}}^{(1)}+E_{\mathrm{n}}^{(1)} \delta_{\mathrm{mn}}
\end{aligned}
$$

## Set $\mathrm{m}=\mathrm{n}$, we have

$$
\boldsymbol{E}_{\mathrm{n}}{ }^{(2)}=\sum_{\mathrm{m} \neq \mathrm{n}}\left|<\psi_{\mathrm{m}}{ }^{(0)}\right| \boldsymbol{H}^{\prime}\left|\psi_{\mathrm{n}}{ }^{(0)}>\right|^{2} /\left[\boldsymbol{E}_{\mathrm{n}}^{(0)-} \boldsymbol{E}_{\mathrm{m}}{ }^{(0)}\right] \quad \text { Eq.(3) }
$$

## Discussion: (Text Book: page 522-527)

a. Eq.(2) shows that the effect of the perturbation on the wave function $\psi_{n}{ }^{(0)}$ is to mix in contributions from the other zero-th order states $\psi_{\mathrm{m}}{ }^{(0)} \mathrm{m} \neq \mathrm{n}$. Because of the factor $1 /\left(E_{\mathrm{n}}{ }^{(0)}-E_{\mathrm{m}}{ }^{(0)}\right)$, the most important contributions to the $\psi_{n}{ }^{(1)}$ come from the states nearest in energy to state $n$.
b. To evaluate the first-order correction in energy, we need only to evaluate a single integral $H^{\prime}$; ; to evaluate the second-order energy correction, we must evalute the matrix elements $\boldsymbol{H}^{\prime}$ between the n -th and all other states m .
c. The summation in Eq.(2), (3) is over all the states, not the energy levels.

## Moller-Plesset (MP) Perturbation Theory

The MP unperturbed Hamiltonian $\boldsymbol{H}^{0}$

$$
\boldsymbol{H}^{0}=\sum_{\mathrm{m}} \boldsymbol{F}(\boldsymbol{m})
$$

where $F(m)$ is the Fock operator for electron $m$. And thus, the perturbation $\boldsymbol{H}$

$$
\boldsymbol{H}=\boldsymbol{H}-\boldsymbol{H}^{0}
$$

Therefore, the unperturbed wave function is simply the Hartree-Fock wave function $\Phi$.

## Ab initio methods: MP2, MP4

## Example One:

Consider the one-particle, one-dimensional system with potential-energy function

$$
\begin{array}{ll}
V=b & \text { for } L / 4<x<3 L / 4, \\
V=0 & \text { for } 0<x \leq L / 4 \& 3 L / 4 \leq x<L
\end{array}
$$

and $V=\infty$ elsewhere. Assume that the magnitude of $b$ is small, and can be treated as a perturbation. Find the first-order energy correction for the ground and first excited states. The unperturbed wave functions of the ground and first excited states are $\psi_{1}=(2 / L)^{1 / 2} \sin (\pi x / L)$ and $\psi_{2}=(2 / L)^{1 / 2} \sin (2 \pi x / L)$, respectively.

## Example Two:

As the first step of the Moller-Plesset perturbation theory, Hartree-Fock method gives the zeroth-order energy. Is the above statement correct?

## Example Three:

Show that, for any perturbation $H^{\prime}, E_{1}{ }^{(0)}+E_{1}{ }^{(1)} \geq E_{1}$ where $E_{1}{ }^{(0)}$ and $E_{1}{ }^{(1)}$ are the zero-th order energy and the first order energy correction, and $E_{1}$ is the ground state energy of the full Hamiltonian $H^{0}+H^{\prime}$.

## Example Four:

Calculate the bond orders of $\mathrm{Li}_{2}$ and $\mathrm{Li}_{2}{ }^{+}$.

| Ground State |  | Excited State | CPU Time Correlation Geometry Size Consistent $\left(\mathrm{CH}_{3} \mathrm{NH}_{2}, 6-31 \mathrm{G}^{*}\right)$ |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| HFSCF | $\sqrt{ }$ |  | 1 | 0 | OK | $\sqrt{ }$ |
| DFT | $\sqrt{ }$ | $\times$ | $\sim 1$ |  | $\checkmark$ | $\sqrt{ }$ |
| CIS | $\times$ | $\sqrt{ }$ | $<10$ |  | OK | $\times$ |
| CISD | $\checkmark$ | $\sqrt{ }$ | 17 | 80-90\% | $\checkmark$ | $\times$ |
| CISDTQ | $\checkmark$ | $\sqrt{ }$ | very large | ( 20 electrons) $\mathbf{9 8 - 9 9 \%}$ | $\checkmark$ | $\times$ |
| MP2 | $\sqrt{ }$ | $\times$ | 1.5 | 85-95\% | $\sqrt{ }$ | $\sqrt{ }$ |
|  |  |  |  | (DZ+P) |  |  |
| MP4 | $\sqrt{ }$ | $\times$ | 5.8 | >90\% | $\sqrt{ }$ | $\sqrt{ }$ |
| CCD | $\sqrt{ }$ | $\times$ | large | >90\% | $\sqrt{ }$ | $\sqrt{ }$ |
| CCSDT | $\sqrt{ }$ | $\times$ | very large | ~100\% | $\sqrt{ }$ | $\sqrt{ }$ |

## Statistical Mechanics

Content:
Ensembles and Their Distributions
Quantum Statistics
Canonical Partition Function
Non-Ideal Gas
References:

1. Grasser \& Richards, "An Introduction to Statistical Thermodynamcis"
2. Atkins, "Physical Chemistry"

## Ensembles and Their Distributions

## State Functions

The value of a state function depends only on the current state of the system. In other words, a state function is some function of the state of the system.


## E, N, T, Y, P, ......

## State Functions:

$$
E, N, T, V, P
$$

When a system reaches its equilibrium, its state functions $E, N, T, V, P$ and others no longer vary.

## Ensemble

An ensemble is a collection of systems.
A Thought Experiment to construct an ensemble
To set up an ensemble, we take a closed system of specific volume, composition, and temperature, and then, replicate it $A$ times. We have $A$ such systems. The collection of these systems is an ensemble. The systems in an ensemble may or may not exchange energy, molecules or atoms.


$\square$ Constant N, E

Microcanonical Ensemble

## -



## Constant N

## Canonical Ensemble



Grant Canonical Ensemble

Microcanonical Ensemble: N, V, E are common; Canonical Ensemble: $\quad N, V, T$ are common;
Grand Canonical Ensemble: $\mu, V, T$ are common.

Microcanonical System: N, E are fixed;
Canonical System:
$N$ is fixed, but $E$ varies;
Grand Canonical System: N, E vary.

## Example:

What kind of system is each of the following systems: (1) an isolated molecular system; (2) an equilibrium system enclosed by a heat conducting wall; (3) a pond; (4) a system surrounded by a rigid and insulating material.

## Principle of Equal A Priori Probabilities

Probabilities of all accessible states of an isolated system are equal.

For instance, four molecules in a three-level system: the following two conformations have the same probability.


## Configurations and Weights

Imagine that an ensemble contains total $A$ systems among which $a_{1}$ systems with energy $E_{1}$ and $N_{1}$ molecules, $a_{2}$ systems with energy $E_{2}$ and $N_{2}$ molecules, $a_{3}$ systems with energy $E_{3}$ and $N_{3}$ molecules, with energy $\varepsilon_{1}$, and so on. The specific distribution of systems in the ensemble is called configuration of the system, denoted as
$\left\{a_{1}, a_{2}, a_{3}, \ldots \ldots.\right\}$.

A configuration $\left\{a_{1}, a_{2}, a_{3}, \ldots \ldots.\right\}$ can be achieved in $W$ different ways, where $W$ is called the weight of the configuration. And $W$ can be evaluated as follows,

$$
W=A!/\left(a_{1}!a_{2}!a_{3}!\ldots\right)
$$

## Distribution of a Microcanonical Ensemble

| State | 1 | 2 | 3 | $\ldots$ | k | $\ldots$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| Energy | $E$ | $E$ | $E$ | $\ldots$ | $E$ | $\ldots$ |
| Occupation | $a_{1}$ | $a_{2}$ | $a_{3}$ | $\ldots$ | $a_{\mathrm{k}}$ | $\ldots$ |

Constraint $\quad \sum_{\mathrm{i}} a_{\mathrm{i}}=A$

$$
W=A!/ a_{1}!\quad a_{2}!a_{3}!\ldots
$$

To maximize $\ln W$ under the constraint, we construct a Lagrangian
$L=\ln W+\alpha \sum_{\mathrm{i}} a_{\mathrm{i}}$
Thus,

$$
0=\partial L / \partial a_{i}=\partial \ln W / \partial a_{i}+\alpha
$$

Utilizing the Stirling's approximation,
$\ln \mathrm{x}!=\mathrm{x} \ln \mathrm{x}-\mathrm{x}$
$\partial \ln W / \partial a_{i}=-\ln a_{\mathrm{i}} / A=-\alpha$,
the probability of a system being found in state $i$,

$$
p_{\mathrm{i}}=a_{\mathrm{i}} / \boldsymbol{A}=\exp (\alpha)=\text { constant }
$$

or, in another word, the probabilities of all states with the same energy are equal.

## Distribution of a Canonical Ensemble

$\begin{array}{lllllll}\text { State } & 1 & 2 & 3 & \ldots & \mathrm{k} & \ldots \\ \text { Energy } & E_{1} & E_{2} & E_{3} & \ldots & E_{\mathrm{k}} & \ldots \\ \text { Occupation } & a_{1} & a_{2} & a_{3} & \ldots & a_{\mathrm{k}} & \ldots\end{array}$
Constraints:

$$
\begin{aligned}
& \sum_{\mathrm{i}} a_{\mathrm{i}}=A \\
& \sum_{\mathrm{i}} a_{\mathrm{i}} E_{\mathrm{i}}=\xi
\end{aligned}
$$

where, $\xi$ is the total energy in the ensemble.
$W=A!/ a_{1}!\quad a_{2}!a_{3}!\ldots$

To maximize $\ln W$ under the above constraints, construct a Lagrangian
$L=\ln W+\alpha \sum_{\mathrm{i}} a_{\mathrm{i}}-\beta \sum_{\mathrm{i}} a_{\mathrm{i}} E_{\mathrm{i}}$
$0=\partial L / \partial a_{i}=\partial \ln W / \partial a_{i}+\alpha-\beta E_{\mathrm{i}}$
$\ln a_{\mathrm{i}} / A=\alpha-\beta E_{\mathrm{i}}$
the probability of a system being found in state $i$ with the energy $E_{\mathrm{i}}$,

$$
p_{i}=a_{i} / A=\exp \left(\alpha-\beta E_{j}\right)
$$

The above formula is the canonical distribution of a system. Different from the Boltzmann distribution of independent molecules, the canonical distribution applies to an entire system as well as individual molecule. The molecules in this system can be independent of each other, or interact among themselves. Thus, the canonical distribution is more general than the Boltzmann distribution. (note, in the literature the canonical distribution and the Boltzmann distribution are sometimes interchangeable).

## Distribution of a Grand Canonical Ensemble

| State | 1 | 2 | 3 | $\ldots$ | k | $\ldots$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| Energy | $E_{1}$ | $E_{2}$ | $E_{3}$ | $\ldots$ | $E_{\mathrm{k}}$ | $\cdots$ |
| Mol. No. | $N_{1}$ | $N_{2}$ | $N_{3}$ | $\ldots$ | $N_{\mathrm{k}}$ | $\cdots$ |
| Occupation | $a_{1}$ | $a_{2}$ | $a_{3}$ | $\cdots$ | $a_{\mathrm{k}}$ | $\cdots$ |

## Constraints: <br> $$
\begin{aligned} & \sum_{\mathrm{i}} a_{\mathrm{i}}=A \\ & \sum_{\mathrm{i}} a_{\mathrm{i}} E_{\mathrm{i}}=\xi \\ & \sum_{\mathrm{i}} a_{\mathrm{i}} N_{\mathrm{i}}=\eta \end{aligned}
$$

where, $\xi$ and $\eta$ are the total energy and total number of molecules in the ensemble, respectively.

$$
W=A!/ a_{1}!a_{2}!a_{3}!\ldots
$$

To maximize $\ln W$ under the above constraints, construct a Lagrangian

$$
\begin{aligned}
& L=\ln W+\alpha \sum_{\mathrm{i}} a_{\mathrm{i}}-\beta \sum_{\mathrm{i}} a_{\mathrm{i}} E_{\mathrm{i}}-\gamma \sum_{\mathrm{i}} a_{\mathrm{i}} N_{\mathrm{i}} \\
& 0=\partial L / \partial a_{i}=\partial \ln W / \partial a_{i}+\alpha-\beta E_{\mathrm{i}}-\gamma N_{\mathrm{i}} \\
& \ln a_{\mathrm{i}} / A=\alpha-\beta E_{\mathrm{i}}-\gamma N_{\mathrm{i}}
\end{aligned}
$$

the probability of a system being found in state $i$ with the energy $E_{\mathrm{i}}$ and the number of particles $N_{\mathrm{i}}$,

$$
p_{\mathrm{i}}=a_{\mathrm{i}} / A=\exp \left(\alpha-\beta E_{\mathrm{i}}-\mu N_{\mathrm{i}}\right)
$$

The above formula describes the distribution of a grand canonical system, and is called the grand canonical distribution. When $N_{\mathrm{i}}$ is fixed, the above distribution becomes the canonical distribution. Thus, the grand canonical distribution is most general.

## Quantum Statistics

Quantum Particle:
Fermion $\quad(\mathrm{S}=1 / 2,3 / 2,5 / 2, \ldots)$
e.g. electron, proton, neutron, ${ }^{3} \mathrm{He}$ nuclei

Boson ( $\mathrm{S}=0,1,2, \ldots$ )
e.g. deuteron, photon, phonon, ${ }^{4} \mathrm{He}$ nuclei

## Pauli Exclusion Principle:

Two identical fermions can not occupy the same state at the same time.

Question: what is the average number particles or occupation of a quantum state?

## Fermi-Dirac Statistics

System: a fermion's state with an energy \& $(\mu \equiv-\gamma / \beta)$
occupation
energy
probability

## $\mathrm{n}=0$

0
$\exp (0)$


$$
\mathrm{n}=1
$$

$\varepsilon$

$$
\exp [-\beta(\varepsilon-\mu)]
$$

There are only two states because of the Pauli exclusion principle.

Thus, the average occupation of the quantum state $\varepsilon$,

$$
\begin{aligned}
n(\varepsilon) & =\frac{\{0 \times \exp (0)+1 \times \exp [-\beta(\varepsilon-\mu)]\}}{\{\exp (0)+\exp [-\beta(\varepsilon-\mu)]\}} \\
& =\frac{\exp [-\beta(\varepsilon-\mu)]}{\{\exp (0)+\exp [-\beta(\varepsilon-\mu)]\}} \\
& =\frac{\exp [-\beta(\varepsilon-\mu)]}{\{1+\exp [-\beta(\varepsilon-\mu)]\}} \\
& =1 /\{\exp [\beta(\varepsilon-\mu)]+\mathbf{1}\}
\end{aligned}
$$

Therefore, the average occupation number $\mathrm{n}(\varepsilon)$ of a fermion state whose energy is $\varepsilon$,

$$
n(\varepsilon)=1 /\{\exp [\beta(\varepsilon-\mu)]+1\}
$$

$\mu$ is the chemical potential. When $\varepsilon=\mu, \mathrm{n}=1 / 2$ For instance, distribution of electrons

## Bose-Einstein Statistics

System: a boson's state with an energy $\varepsilon$

Occupation of the system may be $0,1,2,3, \ldots$, and correspondingly, the energy may be $0, \varepsilon, 2 \varepsilon$, $3 \varepsilon, \ldots$. Therefore, the average occupation of the boson's state,

$$
\begin{aligned}
n(\varepsilon) & =\frac{\{0 \exp (0)+1 \exp [-\beta(\varepsilon-\mu)]+2 \exp [-2 \beta(\varepsilon-\mu)]+3 \exp [-3 \beta(\varepsilon-\mu)]+\ldots\}}{\{\exp (0)+\exp [-\beta(\varepsilon-\mu)]+\exp [-2 \beta(\varepsilon-\mu)]+\exp [-3 \beta(\varepsilon-\mu)]+\ldots\}} \\
& =\frac{\exp [-\beta(\varepsilon-\mu)]}{\{1-\exp [-\beta(\varepsilon-\mu)]\}} \\
& =\mathbf{1} /\{\exp [\boldsymbol{\beta}(\varepsilon-\mu)]-\mathbf{1}\}
\end{aligned}
$$

Therefore, the average occupation number $n(\varepsilon)$ of a boson state whose energy is $\varepsilon$,

$$
n(\varepsilon)=1 /\{\exp [\beta(\varepsilon-\mu)]-1\}
$$

the chemical potential $\mu$ must less than or equal to the ground state energy of a boson, i.e. $\mu \leq \varepsilon_{0}$, where $\varepsilon_{0}$ is the ground state energy of a boson. This is because that otherwise there is a negative occupation which is not physical. When $\mu=\varepsilon_{0}$, $\mathrm{n}(\varepsilon) \rightarrow \infty$, i.e., the occupation number is a macroscopic number. This phenomena is called Bose-Einstein Condensation!
${ }^{4} \mathrm{He}$ superfluid: when $\mathrm{T} \leq \mathrm{T}_{\mathrm{c}}=2.17 \mathrm{~K},{ }^{4} \mathrm{He}$ fluid flows with no viscosity.

## Classical or Chemical Statistics

When the temperature $T$ is high enough or the density is very dilute, $\mathrm{n}(\varepsilon)$ becomes very small, i.e. $\mathrm{n}(\varepsilon) \ll 1$. In another word, $\exp [\beta(\varepsilon-\mu)] \gg 1$. Neglecting +1 or -1 in the denominators, both Fermi-Dirac and Bose-Einstein Statistics become

$$
\mathbf{n}(\varepsilon)=\exp [-\beta(\varepsilon-\mu)]
$$

The Boltzmann distribution!

## Canonical Partition Function

## the canonical distribution

$$
p_{\mathrm{i}}=\exp \left(-\alpha-\beta E_{\mathrm{i}}\right)
$$

Sum over all the states, $\sum_{\mathrm{i}} p_{\mathrm{i}}=1$. Thus,

$$
p_{\mathrm{i}}=\exp \left(-\beta E_{\mathrm{i}}\right) / \mathrm{Q}
$$

where, $\mathrm{Q} \equiv \sum_{\mathrm{i}} \exp \left(-\beta E_{\mathrm{i}}\right)$ is called the canonical partition function.

## An interpretation of the partition function:

If we set the ground state energy $E_{0}$ to zero,
As $T \rightarrow 0, \mathrm{Q} \rightarrow$ the number of ground state, usually 1 ;
As $T \rightarrow \infty, \mathrm{Q} \rightarrow$ the total number of states, usually $\infty$.

## Independent Molecules

Total energy of a state $i$ of the system,

$$
\begin{aligned}
E_{\mathrm{i}}= & \varepsilon_{\mathrm{i}}(1)+\varepsilon_{\mathrm{i}}(2)+\varepsilon_{\mathrm{i}}(3)+\varepsilon_{\mathrm{i}}(4)+\ldots+\varepsilon_{\mathrm{i}}(\mathrm{~N}) \\
\mathrm{Q}= & \sum_{\mathrm{i}} \exp \left[-\beta \varepsilon_{\mathrm{i}}(1)-\beta \varepsilon_{\mathrm{i}}(2)-\beta \varepsilon_{\mathrm{i}}(3)-\beta \varepsilon_{\mathrm{i}}(4)-\ldots\right. \\
& \left.-\beta \varepsilon_{\mathrm{i}}(\mathrm{~N})\right] \\
= & \left\{\sum_{\mathrm{i}} \exp \left[-\beta \varepsilon_{\mathrm{i}}(1)\right]\right\}\left\{\sum_{\mathrm{i}} \exp \left[-\beta \varepsilon_{\mathrm{i}}(2)\right]\right\} \ldots \\
= & \left.\mathrm{q}_{\mathrm{i}} \exp \left[-\beta \varepsilon_{\mathrm{i}}(\mathrm{~N})\right]\right\}
\end{aligned}
$$

## Distinguishable and Indistinguishable Molecules

for distinguishable molecules: $Q=q^{N}$
for indistinguishable molecules: $\mathbf{Q}=\mathbf{q}^{\mathbf{N}} / \mathbf{N}$ !

## Fundamental Thermodynamic Relationships

Relation between energy and partition function

$$
\begin{aligned}
& \mathbf{U}=\mathbf{U}(\mathbf{0})- \\
& (\partial \ln Q / \partial \beta)
\end{aligned}
$$

The Relation between entropy $S$ and partition function $Q$

$$
S=[U-U(O)] / T+k \ln Q
$$

The Helmholtz energy

$$
A-A(\theta)=-k T \ln Q
$$

## The Pressure

$$
p=-(\partial A / \partial V)_{T}
$$

$$
p=k T(\partial
$$

$$
\ln Q / \partial V)_{T}
$$

The Enthalpy

$$
H-H(\theta)=-(\partial \ln Q / \partial \beta)_{V}+k T V(\partial \ln Q / \partial V)_{T}
$$

## The Gibbs energy

$G-G(\theta)=-k T \ln Q+k T V(\partial$
$\ln Q / \partial V)_{T}$

## Non-Ideal Gas

Now let's derive the equation of state for real gases.

Consider a real gas with $N$ monatomic molecules in a volume $V$. Assuming the temperature is $T$, and the mass of each molecule is $m$. So the canonical partition function $Q$ can be expressed as

$$
Q=\sum_{\mathrm{i}} \exp \left(-E_{\mathrm{i}} / k T\right)
$$

where the sum is over all possible state $i$, and $E_{\mathrm{i}}$ is the energy of state $i$.

## In the classical limit, $\mathbf{Q}$ may be expressed as

## $Q=\left(1 / N!h^{3 \mathrm{~N}}\right) \int \ldots \int \exp (-H / k T) \mathrm{dp}_{1} \ldots \mathrm{dp}_{\mathrm{N}} \mathrm{dr}_{1} \ldots$

dr
where, $H=(1 / 2 m) \sum_{i} p_{i}^{2}+\sum_{i>j} V\left(r_{i}, r_{j}\right)$
$Q=(1 / \mathrm{N}!)\left(2 \pi \mathrm{mkT} / \mathrm{h}^{2}\right)^{3 \mathrm{~N} / 2} \mathrm{Z}_{\mathrm{N}}$
$Z_{N}=\int \ldots \int \exp \left(-\sum_{\mathrm{i}>\mathrm{j}} \mathrm{V}\left(\mathrm{r}_{\mathrm{i}}, \mathrm{r}_{\mathrm{j}}\right) / k T\right) \mathrm{dr}_{1} \ldots$ dr
[ note: for ideal gas, $Z_{N}=V^{N}$, and $\left.Q=(1 / \mathrm{N}!)\left(2 \pi \mathrm{mkT} / h^{2}\right)^{3 \mathrm{~N} / 2} V^{\mathrm{V}}\right]$

## The equation of state may be obtained via

## $p=k T(\partial \ln Q / \partial V)_{T}$

We have thus,

$$
\begin{aligned}
\mathbf{p} / \mathbf{k T}=(\partial \ln Q / \partial V)_{T}= & \left(\partial \ln Z_{\mathrm{N}} /\right. \\
\partial V)_{T} & \partial V)_{T}
\end{aligned}
$$

$$
Z_{N}=\int \ldots \int\left\{1+\left[\exp \left(-\sum_{i>j} v\left(r_{i}, r_{j}\right) / k T\right)-1\right]\right\} d r_{1} \ldots d r_{N}
$$

$$
=V^{v}+\int \ldots \int\left[\exp \left(-\sum_{i j} V\left(r_{i}, r_{j}\right) / k T\right)-1\right] d r_{1} \ldots \mathbf{d r}_{N}
$$

$$
\approx V^{N}+(1 / 2) V^{N-2} N(N-1) \iint\left[\exp \left(-V\left(r_{1}, r_{2}\right) / k T\right)-1\right] d r_{1} d r_{2}
$$

$$
\approx V^{N}\left\{1-\left(1 / 2 V^{2}\right) N^{2} \iint\left[1-\exp \left(-\mathrm{V}\left(\mathrm{r}_{1}, \mathrm{r}_{2}\right) / k T\right)\right] \mathrm{dr}_{1} \mathrm{dr}_{2}\right\}
$$

$$
=V^{\mathrm{N}}\left\{1-\mathbf{B} \mathbf{N}^{2} / \mathbf{V}\right\}
$$

where, $B=(1 / 2 V) \iint\left[1-\exp \left(-V\left(r_{1}, r_{2}\right) / k T\right)\right] \mathrm{dr}_{1} \mathrm{dr}_{2}$

Therefore, the equation of state for our gas:

$$
\begin{aligned}
\mathbf{p} / \mathbf{k T} & =\mathbf{N} / \mathbf{V}+(\mathbf{N} / \mathbf{V})^{2} \mathbf{B} \\
& =\mathbf{n}+\mathbf{B} \mathbf{n}^{2}
\end{aligned}
$$

Comparison to the Virial Equation of State
The equation of state for a real gas

$$
P / k T=n+B_{2}(T) n^{2}+B_{3}(T) n^{3}+\ldots
$$

This is the virial equation of state, and the quantities $B_{2}(T), B_{3}(T), \ldots$ are called the second, third, ... virial coefficients.
$\left.\operatorname{xp}\left(\frac{-V\left(r_{12}\right)}{k T}\right)\right] d r_{12}$

## Thus,

$$
\begin{aligned}
B_{2}(T)=B & =\left(\frac{1}{2} V\right) \iint[1- \\
& =\left(\frac{1}{2}\right) \int[1-\mathrm{e}
\end{aligned}
$$

## A. HARD-SPHERE POTENTIAL

$$
\begin{aligned}
& \infty \quad \mathbf{r}_{12}<\sigma \\
& \mathbf{U}\left(\mathbf{r}_{12}\right)= \\
& 0 \quad \mathbf{r}_{12}>\sigma \\
& \begin{aligned}
B_{2}(T) & =(1 / 2) \int_{0} \sigma 4 \pi r^{2} \\
& =2 \pi \sigma^{3} / 3
\end{aligned}
\end{aligned}
$$

## B. SQUARE-WELL POTENTIAL

$$
\begin{aligned}
& \infty \quad \mathbf{r}_{12}<\sigma \\
& \mathbf{U}\left(\mathbf{r}_{12}\right)=-\varepsilon \\
& \sigma<\mathrm{r}_{12}< \\
& \lambda \sigma \\
& 0 \quad \mathrm{r}_{12}>\lambda \sigma \\
& \begin{aligned}
B_{2}(T) & =(1 / 2) \int_{0} \sigma 4 \pi r^{2} \\
& \operatorname{Ar}\left(2 \pi \sigma^{3} / 3\right)\left[1-\left(\lambda^{3}-1\right)\left(e^{\beta \varepsilon}-1\right)\right]
\end{aligned}
\end{aligned}
$$

## C. LENNARD-JONES POTENTIAL

$$
\mathbf{U}(\mathbf{r})=4 \varepsilon\left[(\sigma / \mathbf{r})^{12}-(\sigma / \mathbf{r})^{6}\right]
$$

$\mathbf{B}_{\mathbf{2}}(\mathbf{T})=\left(\frac{1}{2}\right) \int_{0}^{\infty}\left\{\mathbf{1}-\exp \left\{\left(\frac{-4 \varepsilon}{k T}\right)\left[\left.\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6} \right\rvert\,\right\}\right\} \mathbf{4} \mathbf{r}^{\mathbf{2}} \mathbf{d r}\right.$
With

$$
\mathbf{x}=\sigma / \mathbf{r}, \mathbf{T}^{*}=\mathrm{kT} / \varepsilon
$$

$$
\frac{B_{2}(T)}{2 \pi \sigma^{3}}=\int_{0}^{\infty}\left\{1-\exp \left[\left(-4 / \mathbf{T}^{*}\right)\left(\mathbf{x}^{12}-\mathbf{x}^{6}\right)\right]\right\} \mathbf{x}^{2} d x
$$

## Maxwell's Demon (1867)



## Thermal Fluctuation (Smolochowski, 1912)

In his talk "Experimentally Verifiable Molecular Phenomena that Contradict Ordinary Thermodynamics",... Smoluchowski showed That one could observe violations of almost all the usual statements Of the second law by dealing with sufficiently small systems. ... the increase of entropy... The one statement that could be upheld... was the impossibility of perpetual motion of the second kind. No device could be ever made that would use the existing fluctuations to convert heat completely into work on a macroscopic scale ... subject to the same chance fluctuations....

-----H.S. Leff \& A.F. Rex, "Maxwell's Demon"

## Szilard's one-molecule gas model (1929)

To save the second law, a measure of where-about of the molecule produces at least entropy $>k \ln \mathbf{2}$


## Measurement via light signals (L. Brillouin, 1951)

## $h \nu \gg k T$



Figure 5

## A Temporary Resolution !!!???

## Mechanical Detection of the Molecule



Thought experiment illustrating Popper's refutation of Szilard's assignment of an entropy equivalent to physical information.

Figure 12

## Counter-clockwise rotation always !!!

 A Perpetual Machine of second kind ???

Fig. 12. A one-molecule Maxwell's demon ap aratus.

## Demon's memory

## Bennett's solution (1982)

To complete thermodynamic circle, Demon has to erase its memory !!!

Memory eraser needs minimal Entropy production of $\mathrm{k} \ln 2$ (R. Landauer, 1961)


Feynman's Lecture Notes

# Feynman's Ratchet and Pawl System (1961) 

## $\mathrm{T}_{1}=\mathrm{T}_{2}$, no net rotation



## A honeybee stinger



## A Simplest Maxwell's demon



## Average over 200 trajectories No temperature difference!!!



## iiii ${ }^{y} \perp<^{1} \perp$


(e)

Number of particles
in left side


Maxwell's demon
No. of particles: 60
Threshold energy: 20


Our simple demon
No. of particles: 60
The door's moment of inertia: 0.2
Force constant of the string: 10


Feynman's Lecture Notes
rate

Mechanical Rectifier

## Feynman's Ratchet and Pawl System (1961)

$\mathrm{T}_{1}=\mathrm{T}_{2}$, no net rotation
$\mathrm{T}_{1}>\mathrm{T}_{2}$, counter-clockwise rotation
$\mathrm{T}_{1}>\mathrm{T}_{2}$, clockwise rotation


# A two-chamber design: an analogy to Feynman's Ratchet and Pawl 


string


Our two-chamber design



Feynman's ratchet-pawl system

## Feynman's Ratchet and Pawl



$$
\begin{aligned}
& \text { Micro-reversibility } \\
& P(\stackrel{\rightharpoonup}{p}, \vec{q})=P(-\stackrel{\rightharpoonup}{p}, \vec{q})
\end{aligned}
$$

## Determination of temperature at equilibrium



$T_{g a s} \approx T_{\text {ratchet }}$

## Simulation results



The ratchet moves when the leg is cooled down.

## Angular velocity versus $T_{L}-T_{B}$



## The Ratchet and Pawl as an engine



Density of distribution in the phase space

$$
\delta \mathrm{N}=\rho\left(\mathrm{q}_{1} \ldots \mathrm{q}_{\mathrm{f}}, \mathrm{p}_{1} \ldots \mathrm{p}_{\mathrm{f}}\right) \delta \mathrm{q}_{1} \ldots \delta \mathrm{q}_{\mathrm{f}} \delta \mathrm{p}_{1} \ldots \delta \mathrm{p}_{\mathrm{f}}
$$

where $\rho\left(q_{1} \ldots q_{f}, p_{1} \ldots p_{f}\right)$ is fine-grained density at $\left(q_{1} \ldots q_{f}, p_{1} \ldots p_{f}\right)$

Liouville's Theorem: $\mathrm{d} \rho / \mathrm{dt}=0$
Coarse-grained density over $\delta q_{1} \ldots \delta q_{f} \delta p_{1} \ldots \delta p_{f}$ at $\left(q_{1} \ldots q_{\mathrm{f}}, \mathrm{p}_{1} \ldots \mathrm{p}_{\mathrm{f}}\right)$ :
$P=\int \ldots \int \rho\left(q_{1} \ldots q_{f}, p_{1} \ldots p_{f}\right) d q_{1} \ldots d q_{f} d p_{1} \ldots d p_{f} / \delta q_{1} \ldots \delta q_{f} \delta p_{1} \ldots \delta p_{f}$
Boltzmann's H:

$$
H=\int \ldots \int P \log P d q_{1} \ldots \mathrm{dq}_{\mathrm{f}} \mathrm{dp}_{1} \ldots \mathrm{dp}_{\mathrm{f}}
$$

## Boltzmann's H-Theorem

$\mathrm{d}\left(\int \ldots \int \rho \log \rho \mathrm{dq}_{1} \ldots \mathrm{dq}_{\mathrm{f}} \mathrm{dp}_{1} \ldots \mathrm{dp}_{\mathrm{f}}\right) / \mathrm{dt}=0$
$\mathrm{Q}=\rho \log \rho-\rho \log \mathrm{P}-\rho+\mathrm{P} \geq 0$
At $t_{1}, \rho_{1}=P_{1}$

$$
\mathrm{H}_{1}=\int \ldots \int \rho_{1} \log \rho_{1} d q_{1} \ldots \mathrm{dq}_{\mathrm{f}} \mathrm{dp}_{1} \ldots \mathrm{~d} p_{\mathrm{f}}
$$

At $t_{2}, \rho_{2} \neq \mathrm{P}_{2}$
$\mathrm{H}_{2}=\int \ldots \int \mathrm{P}_{2} \log \mathrm{P}_{2} \mathrm{dq}_{1} \ldots \mathrm{dq}_{\mathrm{f}} \mathrm{dp}_{1} \ldots \mathrm{dp}_{\mathrm{f}}$

$$
\mathrm{H}_{1}-\mathrm{H}_{2} \geq 0
$$



# Non=EMgodiczone 

## Entropy reduction? <br> D.J. Evans et al: Prob(dS)/Prob(-dS) $=\operatorname{Exp}(\mathrm{dS})$





Summing up the two contributions, the DWNT oscillator is found to undergo an entroy reduction of $5.0 k_{B}$ as its axial oscillation reemerges after the hibernation period.

## Entropy [Q: Partition Function] $\mathrm{S}=\mathrm{k} \ln \mathrm{W}=-\mathrm{Nk} \Sigma_{\mathrm{i}} p_{\mathrm{i}} \ln p_{\mathrm{i}}=\mathrm{k} \ln \mathrm{Q}-(\partial \ln \mathrm{Q} / \partial \beta)_{\mathrm{V}} / \mathrm{T}$

## Inorganic Chemistry

# Bonding and Coordination Chemistry 

# Books to follow <br> Inorganic Chemistry by Shriver \& Atkins Physical Chemistry: Atkins 

## C. R. Raj

C-110, Department of Chemistry

Bonding in s,p,d systems: Molecular orbitals of diatomics, d-orbital splitting in crystal field $\left(\mathrm{O}_{\mathrm{h}}, \mathrm{T}_{\mathrm{d}}\right)$.
Oxidation reduction: Metal Oxidation states, redox potential, diagrammatic presentation of potential data. Chemistry of Metals: Coordination compounds (Ligands \& Chelate effect), Metal carbonyls - preparation stability and application.

Wilkinson's catalyst - alkene hydrogenation
Hemoglobin, myoglobin \& oxygen transport

## CHEMICAL BONDING: A QUANTUM LOOK

$\mathrm{H}_{2} / / \mathrm{Na}^{+} \mathrm{Cl}^{-} / / \mathrm{C}_{60}$
"These diayrs everyohing is higher."


## Failure of Classical Mechanics

- Total energy, $E=1 / 2 \mathbf{m v}^{2}+V(x)$
- $p=m v \quad(p=m o m e n t u m)$
- $E=p^{2} / 2 m+V(x) \quad \ldots \ldots \ldots$. . $E q .1$



## "A moving ball I know it all"

- Newton's second law is a relation between the acceleration $d^{2} x / d t^{2}$ of a particle and the force $F(x)$ it experiences.

$$
\begin{aligned}
& \text { - Therefore, } \mathbf{v}=\mathrm{p} / \mathbf{m} \\
& \text { - Or, } \quad \mathbf{p}^{\bullet}=\mathbf{F}(\mathbf{x})
\end{aligned}
$$

" Hit the ball hard, it will move fast Hit it soft, it will move slow"

- Continuous variation of energy is possible.

Macroscopic World: "Classical Mechanics - the God"


- Certain experiments done in late $19^{\text {th }}$ century and early $20^{\text {th }}$ century gave results, totally at variance with the predictions of classical physics. All however, could be explained on the basis that, classical physics is wrong in allowing systems to possess arbitrary amounts of energy.
- For example, photoelectric effect.


## Max Planck $E=h \nu$

1900 German physicist


A young Max Planck was to give a lecture on radiant heat. When he arrived he inquired as to the room number for the Planck lecture. He was told, "You are much too young to be attending the lecture of the esteemed professor Planck."
"Each electromagnetic oscillator is limited to discrete values and cannot be varied arbitrarily"

Plank had applied energy quantization to the oscillators in the blackbody but had considered the electromagnetic radiation to be wave.

When UV light is shone on a metal plate in a vacuum, it emits charged particles (Hertz 1887), which were later shown to be electrons by J.J. Thomson (1899).


Potentiostat

## Classical expectations

As intensity of light increases, force increases, so KE of ejected electrons should increase.

Electrons should be emitted whatever the frequency $v$ of the light.

## Actual results:

Maximum KE of ejected electrons is independent of intensity, but dependent on $v$

For $v<v_{0}$ (i.e. for frequencies below a cutoff frequency) no electrons are emitted

## Photoelectric Effect



## Photoelectric Effect.


frequency
(i) No electrons are ejected, regardless of the intensity of the radiation, unless its frequency exceeds a threshold value characteristic of the metal.
(ii) The kinetic energy of the electron increases linearly with the frequency of the incident radiation but is independent of the intensity of the radiation.
(iii) Even at low intensities, electrons are ejected immediately if the frequency is above the threshold.

## Major objections to the <br> Rutherford-Bohr model

-We are able to define the position and velocity of each electron precisely.

- In principle we can follow the motion of each individual electron precisely like planet.
- Neither is valid.


## Werner Heisenberg

Heisenberg's name will always be associated with his theory of quantum mechanics, published in 1925, when he was only 23 years.

- It is impossible to specify the exact position and momentum of a particle simultaneously.
- Uncertainty Principle.
- $\Delta x \quad \Delta \mathrm{p} \geq h / 4 \pi$ where $h$ is Plank's Constant, a fundamental constant with the value $6.626 \times 10^{-34} \mathrm{~J}$ s.

Nobel prize 1921



Einstein was the father of the bomb in two important ways: 1) it was his initiative which started U.S. bomb research; 2) it was his equation $\left(\mathrm{E}=\mathrm{mc}^{2}\right)$ which made the atomic bomb theoretically possible.

Einstein could never accept some of the revolutionary ideas of quantum mechanics. When reminded in 1927 that he revolutionized science 20 years earlier, Einstein replied, "A good joke should not be repeated too often."

Photoelectric Effect

## Einstein

$$
\mathbf{h} v=1 / 2 \mathbf{m} \mathbf{v}^{2}+\phi
$$

- KE $1 / 2 m v^{2}=h v-\phi$
- $\phi$ is the work function
- $h v$ is the energy of the incident light.
- Light can be thought of as a bunch of particles which have energy $E=h \nu$. The light particles are called photons.


## If light can behave as

 particles, why not particles behave as wave?

Louis de Broglie
The Nobel Prize in Physics 1929


French physicist (1892-1987)

## Louis de Broglie

- Particles can behave as wave.
- Relation between wavelength $\lambda$ and the mass and velocity of the particles.
- $\mathbf{E}=\mathbf{h} \nu$ and also $E=m c^{2}$,
- $E$ is the energy
- $m$ is the mass of the particle
- $c$ is the velocity.



## Wave $\longleftrightarrow$ Particle Duality

- $\mathrm{E}=\mathrm{mc}^{2}=\mathrm{h} v$
- $\mathrm{mc}^{2}=\mathrm{h} v$
- $\mathrm{p}=\mathrm{h} / \lambda \quad\{$ since $v=\mathrm{c} / \lambda\}$
- $\lambda=h / p=h / m v$
- This is known as wave particle duality

Flaws of classical mechanics

Photoelectric effect
Heisenberg uncertainty principle limits simultaneous knowledge of conjugate variables

Light and matter exhibit wave-particle duality
Relation between wave and particle properties given by the de Broglie relations

The state of a system in classical mechanics is defined by specifying all the forces acting and all the position and velocity of the particles.

## Wave equation? Schrödinger Equation.

- Energy Levels
- Most significant feature of the Quantum Mechanics: Limits the energies to discrete values.
- Quantization.

God said $\left.-\frac{\hat{b}^{2}}{2 m_{e}} \frac{\partial^{2} \Psi}{\partial z^{2}} \frac{\partial^{2}}{\partial \partial^{2} \Psi} \frac{\partial^{2}}{\partial y^{2}} \frac{\partial^{2} \Psi}{\partial z^{2}}\right)+V(x, y, z) \Psi=E \Psi$
and there was Light!


## The wave function

For every dynamical system, there exists a wave function that is a continuous, square-integrable, single-valued function of the coordinates of all the particles and of time, and from which all possible predictions about the physical properties of the system can be obtained.

Square-integrable means that the normalization integral is finite

If we know the wavefunction we know everything it is possible to know.

## Derivation of wave equation



$$
\begin{gathered}
\text { Time period }=T, \text { Velocity }=v, v=\lambda / T \text {, } \\
\text { Frequency, } v=1 / T, v=v \lambda
\end{gathered}
$$

An Electron Wave is similar to waves of light, sound \& string

## Wave motion of a String: Amplitude vs. Position






1. Maximum displacement $A$
2. Initial condition


Displacement of a particle in SHM
$\mathbf{y}(\mathbf{x})=A \sin 2 \pi \mathrm{x} / \lambda$
A = maximum amplitude
$\mathbf{y}=$ amplitude at point $\mathbf{x}$ at $\mathbf{t}=\mathbf{0}$
At $\mathrm{x}=0, \lambda / 2, \lambda, 3 \lambda / 2,2 \lambda$, the amplitude is 0
At $x=\lambda / 4,5 \lambda / 4,9 \lambda / 4$, the amplitude is maximum.


If the wave is moving to the right with velocity ' $v$ ' at time ' $t$ ' $\mathbf{y}(\mathbf{x}, \mathrm{t})=\mathbf{A} \sin 2 \pi / \lambda(\mathrm{x}-\mathrm{vt})$

$$
\lambda=\mathrm{v} / \nu
$$

- $y=A \sin 2 \pi v(x / v-t)$
- Differentiating y W.R.T $x$, keeping $t$ constant

$$
\delta^{2} y / \delta x^{2}+\left(4 \pi^{2} / \lambda^{2}\right) y=0
$$

## A wave eqn. is born

- In three dimension the wave equation becomes:
- $\delta^{2} \psi / \delta \mathbf{x}^{2}+\delta^{2} \psi / \delta \mathbf{y}^{2}+\delta^{2} \psi / \delta z^{2}+\left(4 \pi^{2} / \lambda^{2}\right) \psi=0$
- It can be written as $\nabla^{2} \psi+\left(4 \pi^{2} / \lambda^{2}\right) \psi=0$
- We have $\lambda=h / m v$
- $\nabla^{2} \psi+\left(4 \pi^{2} m^{2} \mathbf{v}^{2} / h^{2}\right) \psi=0$
- $E=T+V$ or $T=(E-V) \quad(E=$ total energy $)$
- $\mathbf{V}=$ Potential energy, $\mathbf{T}=$ Kinetic energy
- $T=1 / 2 m^{2}=m^{2} \mathbf{v}^{2} / 2 m$
- $m^{2} v^{2}=2 m(E-V)$


## $\nabla^{2} \psi+\left(8 \pi^{2} \mathbf{m} / \mathbf{h}^{2}\right)(\mathbf{E}-\mathbf{V}) \psi=0$

- This can be rearranged as
- $\left\{\left(-\mathbf{h}^{2} / 8 \pi^{2} \mathbf{m}\right) \nabla^{2}+\mathbf{V}\right\} \psi=\mathrm{E} \psi$
- $\mathrm{H} \psi=\mathrm{E} \psi$
- $\mathrm{H}=\left[\left(-h^{2} / 8 \pi^{2} m\right) \nabla^{2}+V\right)$ Hamiltonian operator

$$
\left\{\left(-\mathbf{h}^{2} / 8 \pi^{2} \mathbf{m}\right)\left(\partial^{2} / \partial \mathbf{x}^{2}+\partial^{2} / \partial \mathbf{y}^{2}+\partial^{2} / \partial \mathbf{z}^{2}\right)+\mathbf{V}\right\} \Psi=\mathbf{E} \Psi
$$

$$
\delta^{2} y / \delta x^{2}+\left(4 \pi^{2} / \lambda^{2}\right) y=0
$$

How to write Hamiltonian for different systems?

$$
\left\{\left(-h^{2} / 8 \pi^{2} \mathbf{m}\right) \nabla^{2}+\mathbf{V}\right\} \Psi=\mathbb{E} \Psi
$$

- Hydrogen atom:
- $\mathrm{KE}=1 / 2 \mathrm{~m}\left(\mathbf{v}_{\mathrm{x}}{ }^{2}+\mathbf{v}_{\mathrm{y}}{ }^{2}+\mathrm{v}_{\mathrm{z}}{ }^{2}\right)$
- $P E=-e^{2} / r,(r=$ distance between the electron and the nucleus.)
- $\mathbf{H}=\left\{\left(-h^{2} / 8 \pi^{2} \mathrm{~m}\right) \nabla^{2}-\mathrm{e}^{2} / \mathrm{r}\right\}$
- $\nabla^{2} \Psi+\left(8 \pi^{2} \mathrm{~m} / \mathrm{h}^{2}\right)\left(\mathrm{E}+\mathrm{e}^{2} / \mathbf{r}\right) \Psi=0$
- If the effective nuclear charge is $\mathbf{Z e}$

$$
\text { - } \mathbf{H}=\left\{\left(-h^{2} / 8 \pi^{2} \mathbf{m}\right) \nabla^{2}-\mathbf{Z e} \mathbf{e}^{2} / \mathbf{r}\right\}
$$

## $\mathrm{H}_{2}{ }^{+}$Molecule

$$
\mathbf{e}(\mathbf{x}, \mathbf{y}, \mathbf{z})
$$



the wave function depends on the coordinates of the two nuclei, represented by $R_{A}$ and $R_{B}$, and of the single electron, represented by $r_{1}$.

$$
\begin{gathered}
\mathbf{H}_{\mathbf{2}}^{+} \\
\left\{\left(-\mathrm{h}^{2} / 8 \pi^{2} \mathrm{~m}\right) \nabla^{2}+\mathrm{V}\right\} \Psi=\mathrm{E} \Psi
\end{gathered}
$$


b

- $\mathbf{P E}=\mathrm{V}=-\mathbf{e}^{2} / \mathbf{r}_{\mathrm{a}}-\mathbf{e}^{2} / \mathbf{r}_{\mathrm{b}}+\mathrm{e}^{2} / \mathbf{R}_{\mathrm{ab}}$
- $\mathbf{H}=\left(-h^{2} / 8 \pi^{2} \mathbf{m}\right) \nabla^{2}+\left(-\mathbf{e}^{2} / \mathbf{r}_{\mathrm{a}}-\mathrm{e}^{2} / \mathbf{r}_{\mathrm{b}}+\mathbf{e}^{2} / \mathbf{R}_{\mathrm{ab}}\right)$
- The Wave equation is
- $\nabla^{2} \Psi+\left(8 \pi^{2} \mathbf{m} / \mathbf{h}^{2}\right)\left(\mathbf{E}+\mathbf{e}^{2} / \mathbf{r}_{\mathrm{a}}+\mathrm{e}^{2} / \mathbf{r}_{\mathrm{b}}-\mathbf{e}^{2} / \mathbf{R}_{\mathrm{ab}}\right) \Psi=\mathbf{0}$

Born-Oppenheimer approximation

## $V=-e^{2} / 4 \pi \varepsilon_{0}\left[1 / r_{a}+1 / r_{b}-1 / R_{a b}\right]$

He Atom
e1 $\left(x_{1}, y_{1}, z_{1}\right)$


$$
\left\{\left(-h^{2} / 8 \pi^{2} \mathbf{m}\right) \nabla^{2}+V\right\} \Psi=\mathbb{E} \Psi
$$

- $\mathrm{V}=-2 \mathrm{e}^{2} / \mathrm{r}_{1}-2 \mathrm{e}^{2} / \mathrm{r}_{2}+\mathrm{e}^{2} / \mathrm{r}_{12}$
- $\mathbf{H}=\left(-h^{2} / \mathbf{8} \pi^{2} \mathbf{m}\right)\left(\nabla_{1}{ }^{2}+\nabla_{2}{ }^{2}\right)+V$
- The Wave equation is
- $\left(\nabla_{1}{ }^{2}+\nabla_{2}{ }^{2}\right) \Psi+\left(8 \pi^{2} \mathbf{m} / \mathbf{h}^{2}\right)(\mathbf{E}-\mathrm{V}) \Psi=0$

$$
\begin{aligned}
& \mathbf{e} 1\left(\mathrm{x}_{1}, \mathrm{y}_{1}, \mathrm{z}_{1}\right) \quad \mathrm{r}_{12} \quad \mathrm{e} 2\left(\mathrm{x}_{2}, \mathrm{y}_{2}, \mathrm{z}_{2}\right) \\
& \mathrm{H}_{2} \\
& \begin{array}{l}
\text { A } \\
?
\end{array}
\end{aligned}
$$

- $\mathbf{P E}=\mathbf{V}=$ ?
- $\mathbf{H}=\left(-h^{2} / 8 \pi^{2} \mathbf{m}\right)\left(\nabla_{1}{ }^{2}+\nabla_{2}^{2}\right)+V$
- The Wave equation is
- $\left(\nabla_{1}{ }^{2}+\nabla_{2}{ }^{2}\right) \Psi+\left(8 \pi^{2} \mathrm{~m} / \mathrm{h}^{2}\right)(\mathrm{E}-\mathrm{V}) \Psi=0$


## $\mathrm{V}=-\mathrm{e}^{2} / \mathbf{4} \pi \varepsilon_{0}\left[\mathbf{1} / \mathrm{r}_{\mathrm{a} 1}+\mathbf{1} / \mathrm{r}_{\mathrm{b} 1}+\mathbf{1} / \mathrm{r}_{\mathrm{a} 2}+\mathbf{1} / \mathrm{r}_{\mathrm{b} 2}-1 / \mathrm{r}_{12}-1 / \mathrm{R}_{\mathrm{ab}}\right]$

attractive potential energy Electron-electron repulsion


Internuclear repulsion

## Particle in a box

An electron moving along $x$-axis in a field $V(x)$

$d^{2} \Psi / d x^{2}+8 \pi^{2} \mathrm{~m} / h^{2}(\mathrm{E}-\mathrm{V}) \Psi=0$ Assume $V=0$ between $x=0 \& x=a$

$$
\text { Also } \Psi=0 \text { at } \mathbf{x}=0 \& a
$$

$d^{2} \Psi / d x^{2}+\left[8 \pi^{2} m E / h^{2}\right] \Psi=0$

$$
\begin{gathered}
x=0 \\
m E / h^{2}
\end{gathered}
$$

$d^{2} \Psi / d x^{2}+k^{2} \Psi=0$ where $k^{2}=8 \pi^{2} m E / h^{2}$
Solution is: $\Psi=\mathbf{C} \cos \mathbf{k x}+\mathbf{D} \sin \mathbf{k x}$

- Applying Boundary conditions:
- $\Psi=0$ at $x=0 \Rightarrow C=0$
$\therefore \Psi=\mathbf{D} \sin k x$
- $\Psi=\mathbf{D} \sin \mathbf{k x}$
- Applying Boundary Condition:
- $\Psi=0$ at $x=a, \therefore D \sin k a=0$
- $\sin \mathrm{ka}=0$ or ka $=m \pi$,
- $\mathbf{k}=\mathbf{n} \pi / \mathbf{a}$
- $n=0,1,2,3,4 \ldots$
- $\Psi_{n}=D \sin (m \pi / a) x$
- $k^{2}=8 \pi^{2} m / h^{2}[E]$ or $E=k^{2} h^{2} / 8 \pi^{2} m$
- $E=n^{2} h^{2} / 8 m a^{2}$

$$
\mathbf{k}^{2}=\mathbf{n}^{2} \pi^{2} / \mathbf{a}^{2}
$$

- $n=0$ not acceptable: $\Psi_{n}=0$ at all $x$
- Lowest kinetic Energy $=\mathrm{E}_{0}=\mathbf{h}^{2} / 8 \mathrm{ma} \mathbf{a}^{2}$


## An Electron in One Dimensional Box

$$
\begin{aligned}
& \mathbf{V}=\infty \underset{\sim}{\longleftrightarrow} \mathbf{a}=\infty \quad \cdot \Psi_{\mathrm{n}}=\mathbf{D} \sin (n \pi / \mathbf{a}) \mathbf{x} \\
& \text { - } \mathrm{E}_{\mathrm{n}}=\boldsymbol{n}^{2} \mathbf{h}^{2} / 8 \mathrm{ma}^{2} \\
& \text { - } n=1,2,3, \ldots \\
& \text { - } \mathrm{E}=\mathrm{h}^{2} / 8 \mathrm{ma}^{2}, \mathrm{n}=1 \\
& \text { - } \mathrm{E}=\mathbf{4 h}^{2} / \mathbf{8} \mathrm{ma}^{2}, \mathrm{n}=\mathbf{2} \\
& \text { - } \mathrm{E}=9 \mathrm{~h}^{2} / 8 \mathrm{ma}^{2}, \mathrm{n}=3 \\
& \overline{x=0} \quad \mathbf{x}=\mathbf{a} \\
& \text { Energy is quantized }
\end{aligned}
$$

## Characteristics of Wave Function

He has been described as a moody and impulsive person. He would tell his student, "You must not mind my being rude. I have a resistance against accepting something new. I get angry and swear but always accept after a time if it is right."

## MAX BORN



## Characteristics of Wave Function:

What Prof. Born Said

- Heisenberg's Uncertainty principle: We can never know exactly where the particle is.
- Our knowledge of the position of a particle can never be absolute.
- In Classical mechanics, square of wave amplitude is a measure of radiation intensity
- In a similar way, $\psi^{2}$ or $\psi \psi^{*}$ may be related to density or appropriately the probability of finding the electron in the space.


## The wave function $\Psi$ is the probability amplitude



If the wavefunction of a particle has the value $\psi$ at some point $x$, then the probability of finding the particle between $x$ and $x+\mathrm{d} x$ is proportional to $|\psi|^{2} \mathrm{~d} x$.


If the wavefunction of a particle has the value $\psi$ at some point $r$, then the probability of finding the particle in an infinitesimal volume $\mathrm{d} \tau=\mathrm{d} x \mathrm{~d} y \mathrm{~d} z$ at that point is proportional to $|\psi|^{2} \mathrm{~d} \tau$.


The sign of the wave function has not direct physical significance: the positive and negative regions of this wave function both corresponds to the same probability distribution. Positive and negative regions of the wave function may corresponds to a high probability of finding a particle in a region.

## Characteristics of Wave Function: What Prof. Born Said

- Let $\rho(x, y, z)$ be the probability function,

$$
\cdot \int \rho d \tau=1
$$

Let $\Psi(x, y, z)$ be the solution of the wave equation for the wave function of an electron. Then we may anticipate that
$\rho(x, y, z) \propto \Psi^{2}(x, y, z)$

- choosing a constant in such a way that $\propto$ is converted to =
- $\rho(\mathbf{x}, \mathrm{y}, \mathrm{z})=\Psi^{2}(\mathbf{x}, \mathbf{y}, \mathbf{z})$
$\therefore \quad \int \Psi^{2} d \tau=1$

The total probability of finding the particle is 1 . Forcing this condition on the wave function is called normalization.

- $\int \Psi^{2} \mathbf{d} \tau=1 \quad$ Normalized wave function
- If $\Psi$ is complex then replace $\Psi^{2}$ by $\Psi \Psi^{*}$
- If the function is not normalized, it can be done by multiplication of the wave function by a constant N such that
- $\mathbf{N}^{2} \int \Psi^{2} \mathbf{d} \tau=1$
- $\mathbf{N}$ is termed as Normalization Constant


## Acceptable wave functions

The wave equation has infinite number of solutions, all of which do not corresponds to any physical or chemical reality.

- For electron bound to an atom/molecule, the wave function must be every where finite, and it must vanish in the boundaries
- Single valued
- Continuous
- Gradient ( $\mathrm{d} \Psi / \mathrm{dr}$ ) must be continuous
- $\Psi \Psi * d \tau$ is finite, so that $\Psi$ can be normalized
- Stationary States
- $E=$ Eigen Value $; \Psi$ is Eigen Function


# Need for Effective Approximate Method of Solving the Wave Equation 

- Born Oppenheimer Principle.
- How can we get the most suitable approximate wave function?
- How can we use this approximate wave function to calculate energy $E$ ?


## Operators

"For every dynamical variables there is a corresponding operator"

$\downarrow$
Operators $\longrightarrow$ Symbols for mathematical operation

## Eigen values

The permissible values that a dynamical variable may have are those given by

$$
\alpha \phi=a \phi
$$

$\phi$ - eigen function of the operator $\alpha$ that corresponds to the observable whose permissible values are a

$$
\begin{array}{ll}
\alpha & \text {-operator } \\
\phi \text {-wave function } \\
\text { a } & \text { - eigen value }
\end{array}
$$

$$
\alpha \phi=a \phi
$$

If performing the operation on the wave function yields original function multiplied by a constant, then $\phi$ is an eigen function of the operator $\alpha$
$\phi=e^{2 x}$ and the operator $\alpha=d / d x$
Operating on the function with the operator
$\mathrm{d} \phi / d x=2 \mathrm{e}^{2 \mathrm{x}}=$ constant. $\mathrm{e}^{2 \mathrm{x}}$
$\mathrm{e}^{2 \mathrm{x}}$ is an eigen function of the operator $\boldsymbol{\alpha}$

For a given system, there may be various possible values.

As most of the properties may vary, we desire to determine the average or expectation value. We know

$$
\alpha \phi=a \phi
$$

Multiply both side of the equation by $\phi^{*}$
$\phi^{*} \alpha \phi=\phi^{*} a \phi$
To get the sum of the probability over all space $\int \phi * \alpha \phi \mathrm{~d} \tau=\int \phi^{*} a \phi \mathrm{~d} \tau$
a - constant, not affected by the order of operation

Removing ' $a$ ' from the integral and solving for ' $a$ '

$$
\mathbf{a}=\int \phi^{*} \alpha \phi \mathbf{d} \tau / \int \phi^{*} \phi \mathbf{d} \tau
$$

$\alpha$ cannot be removed from the integral.

$$
\mathbf{a}=<\phi|\alpha| \phi>/<\phi \mid \phi>
$$

## Variation Method: Quick way to get E

- $\mathbf{H} \Psi=\mathbf{E} \Psi$
- $\Psi \mathbf{H} \Psi=\Psi \mathbf{E} \Psi=\mathbf{E} \Psi \Psi$
- If $\Psi$ is complex,
- $\mathbf{E}=\int \Psi^{*} \mathbf{H} \Psi \mathbf{d} \tau / \int \Psi^{*} \Psi \mathbf{d} \tau$
- $\mathbf{E}=<\Psi|\mathbf{H}| \Psi>/<\Psi \mid \Psi>$
- Bra-Ket notation


## What does $\boldsymbol{E}=\langle\Psi| \mathbf{H}|\Psi\rangle /<\Psi \mid \Psi>$ tell us?

- Given any $\Psi, E$ can be calculated.
- If the wave function is not known, we can begin by educated guess and use Variation Theorem.
$\Psi_{1} \Rightarrow E_{1}$
$\Psi_{2} \Rightarrow E_{2}$
"If a trial wave function is used to calculate the energy, the value calculated is never less than the true energy"
- Variation Theorem.
- $\Psi_{1} \Rightarrow E_{1}$
- $\Psi_{2} \Rightarrow E_{2}$

The Variation Theorem tells that

- $E_{1}, E_{2}>\mathrm{E}_{\mathrm{g}}, \mathrm{E}_{\mathrm{g}}$ true energy of the ground state

$$
\cdot \mathrm{IF}, E_{1}>E_{2},
$$

- Then $E_{2}$ and $\Psi_{2}$ is better approximation to the energy and corresponding wave function $\Psi_{2}$ to the true wave
function

Variation Method: The First Few Steps

- We can chose a whole family of wave function at the same time, like trial function with one or more variable parameters $\mathrm{C}_{1}, \mathrm{C}_{2}, \mathrm{C}_{3}, \ldots$
- Then $E$ is function of $\mathrm{C}_{1}, \mathrm{C}_{2}, \mathrm{C}_{3} \ldots \ldots$. .etc.
- $C_{1}, C_{2}, C_{3} \ldots$ etc. are such that $E$ is minimized with respect to them.
- We will utilize this method in explaining chemical bonding.


## Chemical Bonding

- Two existing theories,
- Molecular Orbital Theory (MOT)
- Valence Bond Theory (VBT)


## Molecular Orbital Theory

- MOT starts with the idea that the quantum mechanical principles applied to atoms may be applied equally well to the molecules.


## Н-С르-Н <br> Bondling in ethyne

MOT: We can write the following principles
$\triangle$ Describe Each electron in a molecule by a certain wave function $\Psi$ - Molecular Orbital (MO).
$\triangle$ Each $\Psi$ is defined by certain quantum numbers, which govern its energy and its shape.
$\triangle$ Each $\Psi$ is associated with a definite energy value.
$\triangle$ Each electron has a spin, $\pm 1 / 2$ and labeled by its spin quantum number $\mathrm{m}_{\mathrm{s}}$.
$\boxtimes$ When building the molecule- Aufbau Principle (Building Principle) - Pauli Exclusion Principle.

## Simplest possible molecule: $\mathrm{H}_{2}{ }^{+}$: 2 nuclei and 1 electron.

- Let the two nuclei be labeled as $A$ and $B \&$ wave functions as $\Psi_{\mathrm{A}} \& \Psi_{\mathrm{B}}$.
- Since the complete MO has characteristics separately possessed by $\Psi_{\mathrm{A}}$ and $\Psi_{\mathrm{B}}$,

$$
\begin{aligned}
& \cdot \Psi=C_{A} \Psi_{A}+C_{B} \Psi_{B} \\
& \cdot \operatorname{or} \Psi=N\left(\Psi_{A}+\lambda \Psi_{B}\right)
\end{aligned}
$$

- $\lambda=C_{B} / C_{A}$, and $N$ - normalization constant

This method is known as Linear Combination of Atomic Orbitals or LCAO

- $\Psi_{\mathrm{A}}$ and $\Psi_{\mathrm{B}}$ are same atomic orbitals except for their different origin.
- By symmetry $\Psi_{A}$ and $\Psi_{B}$ must appear with equal weight and we can therefore write
- $\lambda^{2}=1$, or $\lambda= \pm 1$
- Therefore, the two allowed MO's are
- $\Psi=\Psi_{\mathrm{A}} \pm \Psi_{\mathrm{B}}$


## For $\Psi_{A}+\Psi_{B}$ we can now calculate the energy

- From Variation Theorem we can write the energy function as
- $\left.E=\left\langle\Psi_{\mathrm{A}}+\Psi_{\mathrm{B}}\right| \mathrm{H}\left|\Psi_{\mathrm{A}}+\Psi_{\mathrm{B}}>/<\Psi_{\mathrm{A}}+\Psi_{\mathrm{B}}\right| \Psi_{\mathrm{A}}+\Psi_{\mathrm{B}}\right\rangle$

$$
\begin{aligned}
& \text { Looking at the numerator: } \\
& E=\left\langle\Psi_{\mathrm{A}}+\Psi_{\mathrm{B}}\right| \mathrm{H}\left|\Psi_{\mathrm{A}}+\Psi_{\mathrm{B}}>\left|<\Psi_{\mathrm{A}}+\Psi_{\mathrm{B}}\right| \Psi_{\mathrm{A}}+\Psi_{\mathrm{B}}>\right. \\
& \text { - }\left\langle\Psi_{\mathrm{A}}+\Psi_{\mathrm{B}}\right| \mathbf{H}\left|\Psi_{\mathrm{A}}+\Psi_{\mathrm{B}}\right\rangle=\left\langle\Psi_{\mathrm{A}}\right| \mathrm{H}\left|\Psi_{\mathrm{A}}\right\rangle+ \\
& <\Psi_{B}|H| \Psi_{B}>+ \\
& <\Psi_{\mathrm{A}}|\mathbf{H}| \Psi_{\mathrm{B}}>+ \\
& \left\langle\Psi_{\mathrm{B}}\right| \mathrm{H}\left|\Psi_{\mathrm{A}}\right\rangle \\
& \text { - }=\left\langle\Psi_{\mathrm{A}}\right| \mathrm{H}_{\mathrm{H}}\left|\Psi_{\mathrm{A}}\right\rangle+\left\langle\Psi_{\mathrm{B}}\right| \mathrm{H}\left|\Psi_{\mathrm{B}}\right\rangle+2\left\langle\Psi_{\mathrm{A}}\right| \mathrm{H}\left|\Psi_{\mathrm{B}}\right\rangle
\end{aligned}
$$

$=\left\langle\Psi_{\mathrm{A}}\right| \mathrm{H}\left|\Psi_{\mathrm{A}} \gg<\Psi_{\mathrm{B}}\right| \mathrm{H}\left|\Psi_{\mathrm{B}}>+2<\Psi_{\mathrm{A}}\right| \mathrm{H}\left|\Psi_{\mathrm{B}}\right\rangle$
ground state energy of a hydrogen atom. let us call this as $\mathrm{E}_{\mathrm{A}}$

$$
\begin{array}{r}
\left\langle\Psi_{\mathrm{A}}\right| \mathrm{H} \mid \Psi_{\mathrm{B}}>=\left\langle\Psi_{\mathrm{B}}\right| \mathrm{H}\left|\Psi_{\mathrm{A}}\right\rangle=\beta \\
\beta=\text { resonance integral }
\end{array}
$$

$\therefore$ Numerator $=2 \mathrm{E}_{\mathrm{A}}+2 \beta$

Physical Chemistry class test answer scripts will be shown to the students on $3^{\text {rd }}$ March (Tuesday) at $\mathbf{5 : 3 0} \mathbf{~ p m}$ in

Room C-306: Sections 11 and 12

Looking at the denominator:

$$
E=<\Psi_{\mathrm{A}}+\Psi_{\mathrm{B}}|\mathrm{H}| \Psi_{\mathrm{A}}+\Psi_{\mathrm{B}}>/<\Psi_{\mathrm{A}}+\Psi_{\mathrm{B}} \mid \Psi_{\mathrm{A}}+\Psi_{\mathrm{B}}>
$$

$$
\cdot<\Psi_{\mathrm{A}}+\Psi_{\mathrm{B}}\left|\Psi_{\mathrm{A}}+\Psi_{\mathrm{B}}>=<\Psi_{\mathrm{A}}\right| \Psi_{\mathrm{A}}>+
$$

$$
<\Psi_{B} \mid \Psi_{B}>+
$$

$$
<\Psi_{\mathrm{A}} \mid \Psi_{\mathrm{B}}>+
$$

$$
<\Psi_{\mathrm{B}} \mid \Psi_{\mathrm{A}}>
$$

$\cdot=<\Psi_{\mathrm{A}}\left|\Psi_{\mathrm{A}}>+<\Psi_{\mathrm{B}}\right| \Psi_{\mathrm{B}}>+2<\Psi_{\mathrm{A}} \mid \Psi_{\mathrm{B}}>$

$$
=\left\langle\Psi_{\mathrm{A}} \mid \Psi_{\mathrm{A}}\right\rangle+\left\langle\Psi_{\mathrm{B}} \mid \Psi_{\mathrm{B}}\right\rangle+2\left\langle\Psi_{\mathrm{A}} \mid \Psi_{\mathrm{B}}\right\rangle
$$

$\Psi_{\mathrm{A}}$ and $\Psi_{\mathrm{B}}$ are normalized, so $\left\langle\Psi_{A} \mid \Psi_{A}\right\rangle=\left\langle\Psi_{B} \mid \Psi_{B}\right\rangle=1$

$$
\begin{gathered}
\left\langle\Psi_{\mathrm{A}} \mid \Psi_{\mathrm{B}}\right\rangle=\left\langle\Psi_{\mathrm{B}} \mid \Psi_{\mathrm{A}}\right\rangle=\mathbf{S}, \\
\mathbf{S}=\text { Overlap integral. }
\end{gathered}
$$

$\therefore$ Denominator $=2(1+S)$


## Denominator $=2(1+S)$

$$
\begin{gathered}
E_{+}=\left(\mathbf{E}_{\mathbf{A}}+\beta\right) /(1+\mathbf{S}) \\
\text { Also } E_{-}=\left(\mathbf{E}_{\mathbf{A}}-\beta\right) /(1-S)
\end{gathered}
$$

S is very small $\therefore$ Neglect S

$$
\boldsymbol{E}_{ \pm}=\mathbf{E}_{\mathbf{A}} \pm \beta
$$

## Energy level diagram



## Linear combination of atomic orbitals

## Rules for linear combination

1. Atomic orbitals must be roughly of the same energy.
2. The orbital must overlap one another as much as possible- atoms must be close enough for effective overlap.
3. In order to produce bonding and antibonding MOs, either the symmetry of two atomic orbital must remain unchanged when rotated about the internuclear line or both atomic orbitals must change symmetry in identical manner.

## Rules for the use of MOs

* When two AOs mix, two MOs will be produced
* Each orbital can have a total of two electrons
(Pauli principle)
* Lowest energy orbitals are filled first (Aufbau principle)
* Unpaired electrons have parallel spin (Hund's rule)

Bond order $=1 / 2$ (bonding electrons $\boldsymbol{-}$ antibonding electrons)

## Linear Combination of Atomic Orbitals (LCAO)

The wave function for the molecular orbitals can be approximated by taking linear combinations of atomic orbitals.


$$
\psi_{A B}=\mathbf{N}\left(\mathbf{c}_{\mathrm{A}} \psi_{\mathrm{A}}+\mathbf{c}_{\mathrm{B}} \psi_{\mathrm{B}}\right)
$$

$c-$ extent to which each AO contributes to the MO

Probability density
Overlap integral

## Constructive interference



## What holds the molecule together?

- There is nothing magic about the molecule being bonded
- Electrons preferentially spend time between the two nuclei. They act as electrostatic "glue"

$$
\psi_{\mathrm{AB}}^{2}=\left(\mathrm{c}_{\mathrm{A}}^{2} \psi_{\mathrm{A}}^{2}+2 \mathrm{c}_{\mathrm{A}} \mathrm{c}_{\mathrm{B}} \psi_{\mathrm{A}} \psi_{\mathrm{B}}+\mathrm{c}_{\mathrm{B}}^{2} \psi_{\mathrm{B}}^{2}\right)
$$



The accumulation of electron density between the nuclei put the electron in a position where it interacts strongly with both nuclei.

Nuclei are shielded from each other

The energy of the molecule is lower


## Destructive interference

Nodal plane perpendicular to the $\mathbf{H}-\mathrm{H}$ bond axis (en density $=0$ ) Energy of the en in this orbital is higher.


$\mathrm{c}_{\mathrm{A}}=+1, \mathrm{c}_{\mathrm{B}}=-1$

$$
\psi_{\mathrm{u}}=\mathrm{N}\left[\psi_{\mathrm{A}}-\psi_{\mathrm{B}}\right]
$$

Waves cancel


## Amplitudes of wave functions

subtracted.

(b)
$\square$ The electron is excluded from internuclear region $\rightarrow$ destabilizing

Antibonding

When 2 atomic orbitals combine there are 2 resultant orbitals.

Eg. s orbitals
high energy antibonding orbital

Molecular orbitals

low energy bonding orbital


Molecular potential energy curve shows the variation of the molecular energy with internuclear separation.

## Looking at the Energy Profile

- Bonding orbital
- called 1s orbital
- $s$ electron
- The energy of 1 s orbital decreases as R decreases
- However at small separation, repulsion becomes large
- There is a minimum in potential energy curve




## The overlap integral

■The extent to which two atomic orbitals on different atom overlaps : the overlap integral

$$
S=\int \psi_{A}^{*} \psi_{B} d \tau
$$



## Bonding


 （ m －9）operlap．

$$
\mathrm{S}=0 \text { nonbonding }
$$

$$
S>0
$$

## The extent to which

## orbitals overlap can be

 evaluated using an overlap integral S.$-\mathrm{S}=0$ indicates that the orbitals do not overlap/interact with one another

- S depends on the symmetry of the orbital

Bond strength depends on the degree of overlap

## Linear combinations of $p_{z}$ orbitals

- Addition of two $p_{z}$ AOs results a bonding $\sigma_{p} \mathrm{MO}$, subtraction will give an antibonding $\sigma_{p}{ }^{*} \mathrm{MO}$ with a nodal plane perpendicular to the bond axis

$$
\Psi_{\sigma}=\frac{1}{\sqrt{2}}\left[\Psi_{2 p_{s}}\left(H_{a}\right)+\Psi_{2_{R}}\left(H_{b}\right)\right]
$$



## Linear combinations of $p_{x}$ and $p_{y}$ orbitals

- Addition of two $p_{x}\left(\right.$ or $p_{y}$ ) AOs results a bonding $\pi_{p} \mathrm{MO}$ containing a nodal plane along the bond axis:
p
$+$

E
- Subtraction results an antibonding $\pi_{\mathrm{p}}^{*}$ MO with two nodal planes: one plane perpendicular and one parallel to the bond axis


(a)

(b)

(c)

(d)


## Homonuclear Diatomics

- MOs may be classified according to:
(i) Their symmetry around the molecular axis.
(ii) Their bonding and antibonding character.
- $\sigma_{1 \mathrm{~s}}<\sigma_{1 \mathrm{~s}}{ }^{*}<\sigma_{2 \mathrm{~s}}<\sigma_{2 \mathrm{~s}}{ }^{*}<\sigma_{2 \mathrm{p}}<\pi_{\mathrm{y}}(2 \mathrm{p})=\pi_{\mathrm{z}}(2 \mathrm{p})$
$<\pi_{\mathrm{y}}{ }^{*}(2 p)=\pi_{\mathrm{z}}{ }^{*}(2 p)<\sigma_{2 p}{ }^{*}$.


## Classifying orbitals by symmetry

- Orbitals in diatomics can be classified according to their rotational symmetry characteristics as $\sigma, \pi$ or $\delta$. These classifications are strictly only valid for diatomics, but we also use them to describe bonds between pairs of atoms in polyatomic molecules.


$$
d x^{2}-d y y^{2} \text { and } d_{x y}
$$

219 The fomation of s atilub from di-
colitil zotrlap. The conbital toe two
nutwally perpendoular nodal plais itat intersect aluyg the in temuden anis.
 species such as $\left[\mathrm{Re}_{2} \mathrm{Cl}_{18}\right]^{2-}$

## Ungerade or gerade ?

- MOs in molecules that are centrosymmetric can be classified as (g) or (u)
- Useful for predicting spectroscopic transitions etc.
- (g) implies that the wavefunction does not change sign on inversion through the center of the molecule. (u) means that it does change sign
$g$ - identical
under inversion
$u$ - not identical

$21 \pi_{\mathrm{g}}$ and $\pi_{\mathrm{u}}$ orbitals


## Place labels $g$ or $u$ in this diagram


(c)

## First period diatomic molecules


$\sigma 1 s^{2}$

Bond order: 1


Diatomic molecules: The bonding in $\mathrm{He}_{2}$

$\sigma 1 s^{2}, \sigma^{*} 1 s^{2}$

Bond order: 0

Molecular Orbital theory is powerful because it allows us to predict whether molecules should exist or not and it gives us a clear picture of the of the electronic structure of any hypothetical molecule that we can imagine.


Full energy
level diagram for second row diatomics

Second period diatomic molecules

$\sigma 1 s^{2}, \sigma^{*} 1 s^{2}, \sigma 2 s^{2}$

Bond order: 1

Diatomic molecules: Homonuclear Molecules of the Second Period


$$
\sigma 1 s^{2}, \sigma^{*} 1 s^{2}, \sigma 2 s^{2}, \sigma^{*} 2 s^{2}
$$

Bond order: 0

## Molecular oxygen



Bond order $=2$
2 unpaired electrons $->$ paramagnetic
Simplified

## Molecular fluorine



Bond order = 1 0 unpaired electrons $->$ diamagnetic

Simplified

## MO diagram for $\mathbf{B}_{2}$



Diamagnetic??

## Orbital Mixing

Orbitals with similar energy interact, if they have the appropriate symmetries

The $\sigma_{2 p}$ and $\sigma_{2 s}$ orbitals are symmetry related and give rise to two new orbitals, one with higher and one with lower energy

Li : $200 \mathrm{~kJ} / \mathrm{mol}$
F: $2500 \mathrm{~kJ} / \mathrm{mol}$


## Effect of orbital mixing



Same symmetry, energy mix-

## MO diagram for $\mathbf{B}_{2}$



Paramagnetic


Diamagnetic
$\mathrm{C}_{2}$


Para ${ }^{\text {agnetic ? }}$

## General MO diagrams


$\mathrm{Li}_{\mathbf{2}}$ to $\mathbf{N}_{\mathbf{2}}$
$\mathrm{O}_{2}$ and $\mathrm{F}_{2}$


## Bond lengths in diatomic molecules



## Bond Order vs. Bond Length \& Energy

| Species | Bond order | Bond length/pm | Bond energy/kJ mol-1 |
| :--- | :---: | :---: | :---: |
| $\mathrm{H}_{2}{ }^{+}$ | $1 / 2$ | 105.2 | 256 |
| $\mathrm{H}_{2}$ | 1 | 74.1 | 432 |
| $\mathrm{H}_{2}$ | $1 / 2$ | - | $100-200$ |
| $\mathrm{He}_{2}$ | 0 | 297 | $0.1^{*}$ |
| $\mathrm{Li}_{2}$ | 1 | 267.3 | 101 |
| $\mathrm{Be}_{2}$ | 0 | - | 4 |
| $\mathrm{~B}_{2}$ | 1 | 159 | 289 |
| $\mathrm{C}_{2}$ | 2 | 124.25 | 599 |
| $\mathrm{~N}_{2}$ | 3 | 109.8 | 942 |
| $\mathrm{O}_{2}$ | 2 | 120.7 | 493 |
| $\mathrm{O}_{2}{ }^{+}$ | $2^{1 / 2}$ | 111.6 | 643 |
| $\mathrm{O}_{2}$ | $1 / 2$ | 135 | 395 |
| $\mathrm{Q}_{2} 2^{-}$ | 1 | 140 | - |
| $\mathrm{F}_{2}$ | 1 | 141.2 | 155 |
| $\mathrm{Ne}_{2}$ | 0 | 310 | $0.2^{*}$ |
| "Van der Waal forces. |  |  |  |

## Summary

From a basis set of $\mathbf{N}$ atomic orbitals, $\mathbf{N}$ molecular orbitals are constructed. In Period 2, $\mathrm{N}=\mathbf{8}$.

The eight orbitals can be classified by symmetry into two sets: $4 \sigma$ and $4 \pi$ orbitals.

The four $\pi$ orbitals from one doubly degenerate pair of bonding orbitals and one doubly degenerate pair of antibonding orbitals.

The four $\sigma$ orbitals span a range of energies, one being strongly bonding and another strongly antibonding, with the remaining two $\sigma$ orbitals lying between these extremes.

To establish the actual location of the energy levels, it is necessary to use absorption spectroscopy or photoelectron spectroscopy.

## Molecular Nitrogen

- According to calculations the $\sigma_{g}$ orbital is higher in energy than the two $\pi_{2 \mathrm{p}}$ orbitals:



## Hetronuclear diatomics

- The contributions to the MO from each of the atoms is unequal

$$
-\psi=c_{A} \phi(\mathrm{~A})+\mathrm{c}_{\mathrm{B}} \phi(\mathrm{~B})+\ldots \ldots .
$$

- The more electronegative atom contributes strongly to the bonding orbital
- The less electronegative atom contributes strongly to the anti-bonding orbital - gives rise to polarity Distance between b-MO and AO


## Heteronuclear Diatomics....

The energy level diagram is not symmetrical.
The bonding MOs are closer to the atomic orbitals which are lower in energy.
$\triangle$ The antibonding MOs are closer to those higher in energy.
c - extent to which each atomic orbitals contribute to MO


If $c_{A}>c_{B}$ the MO is composed principally of $\phi_{A}$

HF

## $3 \sigma$

## Mainly H

## Largely nonbonding

## HF

$$
\begin{array}{ll}
\text { 1s } & 1 \\
\text { 2s, } 2 \mathrm{p} & 7
\end{array}
$$

$$
\mathrm{H} 1 \mathrm{~s}
$$

$\psi=c_{1} \phi_{\mathrm{H} 1 \mathrm{~s}}+\mathrm{c}_{2} \phi_{\mathrm{F} 2 \mathrm{~s}}+\mathrm{c}_{3} \phi_{\mathrm{F} 2 \mathrm{pz}}$

## $\mathbf{2} \mathbf{p}_{\mathrm{x}}$ and $\mathbf{2 p}_{\mathrm{y}}$

$1 \sigma^{2} 2 \sigma^{2} 1 \pi^{4}$
Polar

# Exclusively F 

Mainly F

