Simultaneous Eigenfunctions
- commuting observables
- linear combinations of degenerate states
- symmetry + spin

Pauli Principle

He-2 repulsion - MO vs VB picture

We use observables to define wavefunctions.

Complete set of commuting observables (CSCO)

\[ \psi_1, \psi_2 \]
\[ \psi_3, \psi_4 \]

\[ \hat{H} \]
\[ \hat{I} \]

Different energetics

Different symmetry w.r.t. inversion.

These four wavefunctions can be completely characterized by specifying their energy and symmetry w.r.t. inversion (\(S\) or \(U\)).

Ex: H atom \([\hat{H}, L^2, L_z, \text{spin}]\)

A wavefunction is specified by its eigenvalues for these operators - \(\psi_{\text{eigen}}\).
we must pick our operators so that we can have eigenfunctions of all of them simultaneously.
For this to be possible, our operators must commute. $\hat{A}\hat{B} = \hat{B}\hat{A}$ or $[A,B] = 0$.

Simple case - all eigenvalues are distinct, no degenerate states.

If $\varphi$ is an eigenfunction of $\hat{A}$ and $\hat{B}$ and $\hat{A}$ commute, then

$\hat{A}\varphi = \lambda\varphi \rightarrow \hat{B}\hat{A}\varphi = \hat{B}\lambda\varphi$
$\hat{A}(\hat{B}\varphi) = \lambda(\hat{B}\varphi)$

Since there $\hat{B}\varphi = b\varphi$

are no degenerate states, $\hat{B}\varphi$ can only differ from $\varphi$ by a multiplicative constant. So $\varphi$ is also an eigenfunction of $\hat{B}$.

If there are degenerate eigenstates, $\varphi_1, \varphi_2$ at $\hat{A}\varphi_1 = \lambda\varphi_1$ and $\hat{A}\varphi_2 = \lambda\varphi_2$.

Then any linear combination of $\varphi_1$ and $\varphi_2$ is also an eigenstate with eigenvalue $\lambda$.

$\hat{A}(a\varphi_1 + b\varphi_2) = \lambda(a\varphi_1 + b\varphi_2)$
which combinations are eigenfunctions of $\hat{B}$? out of $n$ degenerate states, we can make $n$ eigenfunctions of $\hat{B}$.

\[ \hat{H} = h_1 + h_2 + \frac{1}{\sqrt{2}} \]

\[ \text{ignore this term for now} \]

$\hat{I}$ inversion operator.

$\hat{H}$ is invariant to inversion because all distances stay the same.

\[ \hat{I} (\hat{H}(\vec{r}) \phi(\vec{r})) = \hat{H}(\vec{r}) \phi(-\vec{r}) \]

\[ = \hat{H}(\vec{r}) \hat{I} \phi(\vec{r}) \]

so $\hat{H} \hat{I} = \hat{I} \hat{H}$, these operators commute.

Eigenvalues of $\hat{I}$ are $\pm 1, 0$ or $0$.

**Eigenstates of $\hat{H}$:**

MO wavefunctions

MO products of $1e^-$ wavefunctions

$\phi_g \rightarrow \{ \}$ from $H_2^+$

$\phi_u \rightarrow \{ \}$

$\hat{H} : 2E_g$

$\hat{I} : +1$

$\hat{I} : E_g + E_u$

$H: N/4$
The $u_g$ and $u_u$ wave functions are not eigenstates of $\hat{I}$. We can take linear combinations to get eigenstates.

These are now eigenfunctions of both $\hat{H}$ and $\hat{I}$. If we put the $1/r_2$ term back into $\hat{H}$, we see that the $u_g$-$u_u$ state will have better energy because it has a nodal plane along the $\vec{r}_1 = \vec{r}_2$ line.
we have spin operators $s_x, s_y, s_z$. 

They do not commute with each other. They do commute with $s^2 = s_x^2 + s_y^2 + s_z^2$.

We choose to specify the eigenvalues of $s^2$ and $s_z$. $[s^2, s_z] = 0$.

Eigenfunctions are $\alpha$ and $\beta$.

$$s^2 \{ \alpha \} = \frac{1}{2} (\frac{1}{2} + 1) \{ \alpha \}$$

$$s^2 \{ \beta \} = \frac{1}{2} \{ \alpha \}$$

$s^2 = \frac{1}{2}$, $m_{s^2} = \frac{1}{2}$.

**Multiple Electrons**

We can define $s^2, s_z$ operators for multiple electrons.

$s_z$ eigenvalues just add, so multiplying $\alpha$'s and $\beta$'s gives an eigenfunction of $s_z$.

Can combine $s_z$ eigenfunctions to make an eigenfunction of $s^2$.

$$s^2 = s_+ s_- - s_z^2 + s_z^2$$

$s_+(\beta\beta) = \alpha \beta + \beta \alpha$

$s_-(\beta\alpha) = \beta\beta$. 
Good \( s^2 \) wave functions

\[
\begin{align*}
\alpha \alpha & \quad s = \frac{3}{2} \\
\alpha \beta - \beta \alpha & \quad s = 0 \\
(\alpha \beta - \beta \alpha) \beta & \quad s = \frac{1}{2}
\end{align*}
\]

B90

\[
\alpha \beta \\
(\alpha \beta + \beta \alpha) \beta
\]

2e'-s

\( \gamma \): Transposition operator - interchanges 2 e'-s.

\[ [\gamma, s_z] = [\gamma, s^2] = 0. \]

Good 2 electron spin functions must be eigenfunctions of \( \gamma \).

\[
\begin{array}{ccc}
\alpha \alpha & \gamma & 1 \\
\alpha \beta & 0 & \frac{1}{\sqrt{2}} \\
\beta \alpha & 0 & \frac{1}{\sqrt{2}} \\
\beta \beta & -1 & 1
\end{array}
\]

Use linear combinations:

\[
\begin{array}{ccc}
\alpha \alpha & s_\zeta & \frac{1}{\sqrt{2}} \\
\beta \beta & -1 & 1 \\
\alpha \beta + \beta \alpha & 0 & 1
\end{array}
\]

\[ s = 1 \text{ triplet} \]

\[
\begin{array}{ccc}
\alpha \beta - \beta \alpha & 0 & -1 \\
\alpha \beta + \beta \alpha & 0 & 1
\end{array}
\]

\[ s = 0 \text{ singlet} \]