

# Matrix Representation of Spin Operators

Consider a simple spin-1/2 system, such as an electron, a proton, or a muon.

Take as basis set, the eigenfunctions of  $\hat{S}_z$  :  $\hat{S}_z|\alpha\rangle = \frac{1}{2}|\alpha\rangle$     $\hat{S}_z|\beta\rangle = -\frac{1}{2}|\beta\rangle$

The matrix elements are  $\langle\alpha|\hat{S}_z|\alpha\rangle = \frac{1}{2}$     $\langle\beta|\hat{S}_z|\beta\rangle = -\frac{1}{2}$     $\Rightarrow$   $\hat{S}_z = \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$   
 $\langle\alpha|\hat{S}_z|\beta\rangle = \frac{1}{2}\langle\alpha|\beta\rangle = 0$     $\langle\beta|\hat{S}_z|\alpha\rangle = 0$

Similarly,  $\hat{S}^2|\alpha\rangle = s(s+1)|\alpha\rangle = \frac{3}{4}|\alpha\rangle$     $\Rightarrow$   $\hat{S}^2 = \frac{3}{4}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$     $\hat{S}^2\hat{S}_z = \frac{3}{8}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \hat{S}_z\hat{S}^2$   
 $\hat{S}^2|\beta\rangle = \frac{3}{4}|\beta\rangle$   
 $[\hat{S}^2, \hat{S}_z] = 0$

$\hat{S}_x|\alpha\rangle = \frac{1}{2}|\beta\rangle$     $\hat{S}_x|\beta\rangle = \frac{1}{2}|\alpha\rangle$     $\hat{S}_x = \frac{1}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$     $\hat{S}_y = \frac{1}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$     $\alpha$  and  $\beta$  are not eigenfunctions of  $\hat{S}_x$  and  $\hat{S}_y$   
 $\hat{S}_y|\alpha\rangle = \frac{1}{2}i|\beta\rangle$     $\hat{S}_y|\beta\rangle = -\frac{1}{2}i|\alpha\rangle$

$\hat{S}_x\hat{S}_y = \frac{1}{4}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} = \frac{1}{4}i\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$   
 $\hat{S}_y\hat{S}_x = \frac{1}{4}i\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$     $\Rightarrow$   $[\hat{S}_x, \hat{S}_y] = \frac{1}{2}i\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = i\hat{S}_z$

# Matrix Diagonalization of a Spin Operator

$$\hat{S}_x = \frac{1}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \text{Set up the secular equation:} \quad \det \begin{pmatrix} 0-\lambda & \frac{1}{2} \\ \frac{1}{2} & 0-\lambda \end{pmatrix} = \lambda^2 - \frac{1}{4} = 0 \quad \text{and solve:} \quad \lambda = \pm \frac{1}{2}$$

To find the coefficients of the eigenvectors, write out the simultaneous equations for each eigenvalue. Solve for coefficients and normalize

For  $\lambda = -\frac{1}{2}$

$$\begin{aligned} (0 + \frac{1}{2})c_{11} + \frac{1}{2}c_{12} &= 0 & c_{11} &= -c_{12} & c_{11}^2 + c_{12}^2 &= 1 & c_{11} &= \frac{1}{\sqrt{2}} = -c_{12} \\ \frac{1}{2}c_{11} + (0 + \frac{1}{2})c_{12} &= 0 & & & & & & \end{aligned}$$

For  $\lambda = \frac{1}{2}$

$$\begin{aligned} (0 - \frac{1}{2})c_{21} + \frac{1}{2}c_{22} &= 0 & c_{21} &= c_{22} & c_{21}^2 + c_{22}^2 &= 1 & c_{21} &= \frac{1}{\sqrt{2}} = c_{22} \\ \frac{1}{2}c_{21} + (0 - \frac{1}{2})c_{22} &= 0 & & & & & & \end{aligned}$$

$$\begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} \quad \frac{1}{4} \begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix} = \frac{1}{2} \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$$

or

$$\begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} \quad \frac{1}{4} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

arbitrary labelling of wave functions

↑  
 $\hat{S}_x$  is diagonal in the new basis

# H Atom Spin States – 1

also muonium!

Spin Hamiltonian

in units of  $\hbar$

$$\hat{H} = \omega_e \hat{S}_z - \omega_p \hat{I}_z + \omega_0 \hat{S} \cdot \hat{I}$$

electron
nuclear
← hyperfine interaction  
Zeeman interactions
(isotropic case)

$$\hat{S} \cdot \hat{I} = \hat{S}_x \hat{I}_x + \hat{S}_y \hat{I}_y + \hat{S}_z \hat{I}_z$$

$$\left. \begin{aligned} \hat{S}_+ &= \hat{S}_x + i\hat{S}_y \\ \hat{S}_- &= \hat{S}_x - i\hat{S}_y \end{aligned} \right\} \Leftrightarrow \left. \begin{aligned} \hat{S}_x &= \frac{1}{2}(\hat{S}_+ + \hat{S}_-) \\ \hat{S}_y &= \frac{1}{2i}(\hat{S}_+ - \hat{S}_-) \end{aligned} \right\}$$

$$\hat{S} \cdot \hat{I} = \frac{1}{2}(\hat{S}_+ \hat{I}_- + \hat{S}_- \hat{I}_+) + \hat{S}_z \hat{I}_z$$

$$\begin{aligned} \hat{S}_x \hat{I}_x &= \frac{1}{4}(\hat{S}_+ \hat{I}_+ + \hat{S}_+ \hat{I}_- + \hat{S}_- \hat{I}_+ + \hat{S}_- \hat{I}_-) \\ \hat{S}_y \hat{I}_y &= -\frac{1}{4}(\hat{S}_+ \hat{I}_+ - \hat{S}_+ \hat{I}_- - \hat{S}_- \hat{I}_+ + \hat{S}_- \hat{I}_-) \end{aligned}$$

Consider a basis set of product spin functions

$$|\alpha\alpha\rangle, |\alpha\beta\rangle, |\beta\alpha\rangle \text{ and } |\beta\beta\rangle \quad \equiv |m_S, m_I\rangle$$

$$\begin{aligned} \hat{H}|\alpha\alpha\rangle &= \omega_e \hat{S}_z |\alpha\alpha\rangle - \omega_p \hat{I}_z |\alpha\alpha\rangle + \frac{1}{2}\omega_0 (\hat{S}_+ \hat{I}_- + \hat{S}_- \hat{I}_+) |\alpha\alpha\rangle + \omega_0 \hat{S}_z \hat{I}_z |\alpha\alpha\rangle \\ &= \frac{1}{2}\omega_e |\alpha\alpha\rangle - \frac{1}{2}\omega_p |\alpha\alpha\rangle + 0 + \frac{1}{4}\omega_0 |\alpha\alpha\rangle \end{aligned}$$

$|\alpha\alpha\rangle$  is an eigenfunction

$$\begin{aligned} \hat{H}|\alpha\beta\rangle &= \omega_e \hat{S}_z |\alpha\beta\rangle - \omega_p \hat{I}_z |\alpha\beta\rangle + \frac{1}{2}\omega_0 (\hat{S}_+ \hat{I}_- + \hat{S}_- \hat{I}_+) |\alpha\beta\rangle + \omega_0 \hat{S}_z \hat{I}_z |\alpha\beta\rangle \\ &= \frac{1}{2}\omega_e |\alpha\beta\rangle + \frac{1}{2}\omega_p |\alpha\beta\rangle + \frac{1}{2}\omega_0 (0 + |\beta\alpha\rangle) - \frac{1}{4}\omega_0 |\alpha\beta\rangle \end{aligned}$$

$|\alpha\beta\rangle$  is not an eigenfunction

## H Atom Spin States – 2

Evaluating all matrix elements...

$$\hat{\mathbf{H}} = \begin{pmatrix} \frac{1}{2}\omega_e - \frac{1}{2}\omega_p + \frac{1}{4}\omega_0 & 0 & 0 & 0 \\ 0 & \frac{1}{2}\omega_e + \frac{1}{2}\omega_p - \frac{1}{4}\omega_0 & \frac{1}{2}\omega_0 & 0 \\ 0 & \frac{1}{2}\omega_0 & -\frac{1}{2}\omega_e - \frac{1}{2}\omega_p - \frac{1}{4}\omega_0 & 0 \\ 0 & 0 & 0 & -\frac{1}{2}\omega_e + \frac{1}{2}\omega_p + \frac{1}{4}\omega_0 \end{pmatrix} \begin{matrix} |\alpha\alpha\rangle \\ |\alpha\beta\rangle \\ |\beta\alpha\rangle \\ |\beta\beta\rangle \end{matrix}$$

$$E_1 = \frac{1}{2}\omega_e - \frac{1}{2}\omega_p + \frac{1}{4}\omega_0 \quad |1\rangle = |\alpha\alpha\rangle$$

$$E_4 = -\frac{1}{2}\omega_e + \frac{1}{2}\omega_p + \frac{1}{4}\omega_0 \quad |4\rangle = |\beta\beta\rangle$$

The central block must be diagonalized to find  $E_2$  and  $E_3$ .

$$\left[ \frac{1}{2}(\omega_e + \omega_p) - \frac{1}{4}\omega_0 - E \right] \left[ -\frac{1}{2}(\omega_e + \omega_p) - \frac{1}{4}\omega_0 - E \right] - \frac{1}{4}\omega_0^2 = 0$$

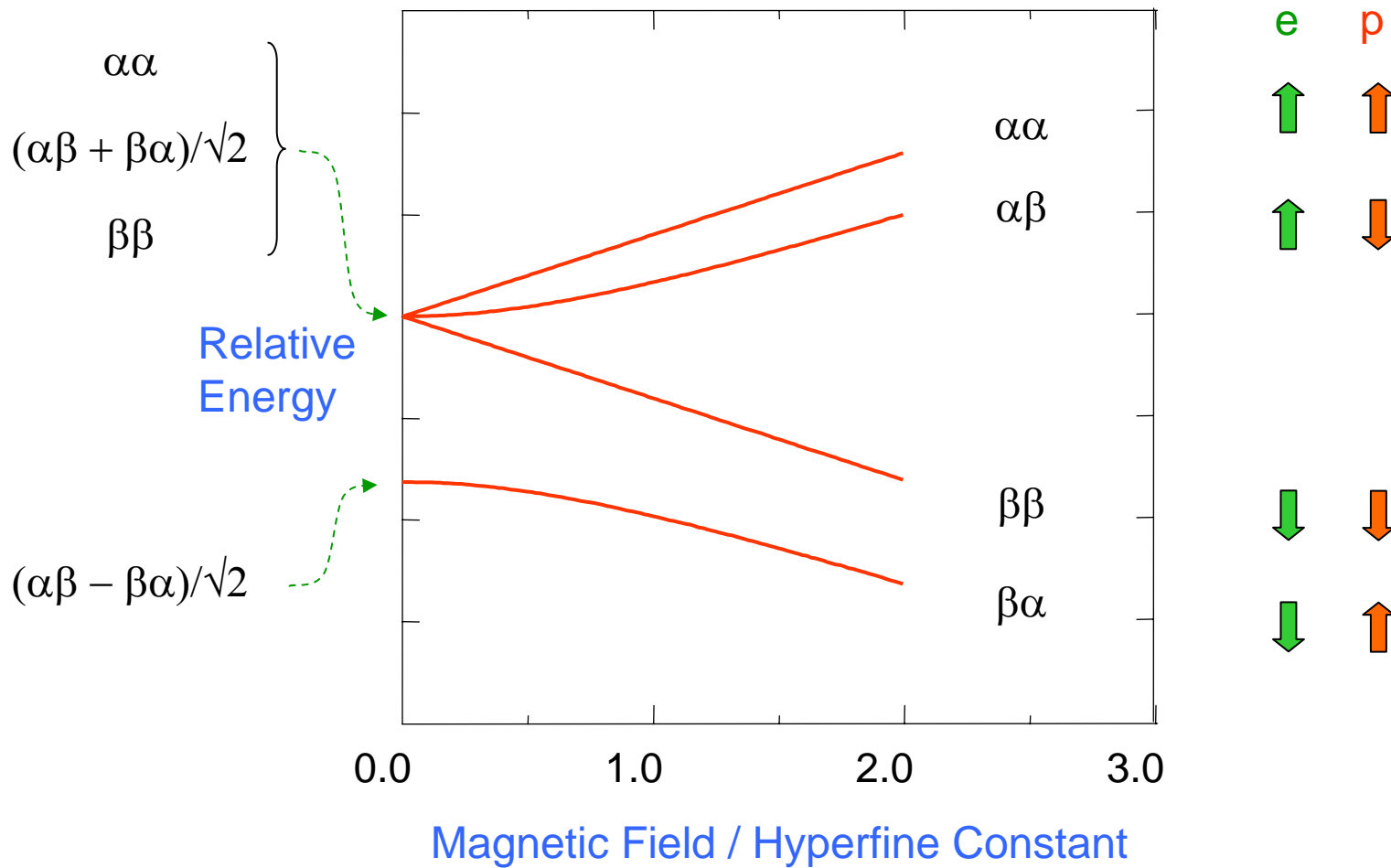
$$E_2 = \frac{1}{2} \left[ (\omega_e + \omega_p)^2 + \omega_0^2 \right]^{1/2} - \frac{1}{4}\omega_0 \quad |2\rangle = c|\alpha\beta\rangle + s|\beta\alpha\rangle$$

$$E_3 = -\frac{1}{2} \left[ (\omega_e + \omega_p)^2 + \omega_0^2 \right]^{1/2} - \frac{1}{4}\omega_0 \quad |3\rangle = c|\beta\alpha\rangle - s|\alpha\beta\rangle$$

$$c^2 + s^2 = 1$$

# Energy levels of a two spin- $\frac{1}{2}$ system

Breit-Rabi diagram



# Perturbation Theory

time-independent theory for non-degenerate states

Used if the Schrödinger equation cannot be solved exactly,  
but the problem is similar to another whose solution is known.

If  $\hat{H} = \hat{H}_0 + \hat{h}$  where  $\hat{H}_0 \psi_n^0 = E_n^0 \psi_n^0$

Approximate  
energies

$$E_j = E_j^0 + \langle \psi_j^0 | \hat{h} | \psi_j^0 \rangle + \sum_{k \neq j} \frac{\langle \psi_j^0 | \hat{h} | \psi_k^0 \rangle \langle \psi_k^0 | \hat{h} | \psi_j^0 \rangle}{E_j^0 - E_k^0}$$

zero order
1st-order correction
2nd-order correction

Approximate  
wave functions

$$\psi_j = \psi_j^0 + \sum_{k \neq j} c_k \psi_k^0 \quad \text{where} \quad c_k = \frac{\langle \psi_k^0 | \hat{h} | \psi_j^0 \rangle}{E_j^0 - E_k^0}$$

The perturbed wave function has *other* eigenfunctions admixed.

The mixing coefficients  $c_k$  depend on the strength of  
the perturbation relative to the energy separation  $E_j^0 - E_k^0$

Does not work  
for  $E_j^0 = E_k^0$  !

If necessary, use linear  
combinations to avoid  
this problem.

# Perturbation Theory – Derivation

$$\hat{H} = \hat{H}^0 + \hat{H}^1 \quad \psi_j = |j\rangle + \sum_{k \neq j} c_k |k\rangle \quad \text{where } |j\rangle, |k\rangle \text{ are eigenfunctions of } \hat{H}^0$$

$$E_j = E_j^0 + E_j^1 + E_j^2 + \dots$$

Take  $\hat{H}\psi_j = E_j\psi_j$  and expand  $\psi_j$ :  $\hat{H}|j\rangle + \sum_{k \neq j} c_k \hat{H}|k\rangle = E_j|j\rangle + E_j \sum_{k \neq j} c_k |k\rangle$

Premultiply by  $\langle j|$ , expand  $\hat{H}$  and use  $\langle j|k\rangle = \delta_{jk}$

$$\hat{H}_{jj}^0 + \hat{H}_{jj}^1 + \sum_{k \neq j} c_k \hat{H}_{jk}^0 + \sum_{k \neq j} c_k \hat{H}_{jk}^1 = E_j$$

$$E_j^0 \quad E_j^1 \quad 0 \quad E_j^2$$

Premultiply by  $\langle i|$   $i \neq j$

$$\hat{H}_{ij}^0 + \hat{H}_{ij}^1 + \sum_{k \neq j} c_k \hat{H}_{ik}^0 + \sum_{k \neq j} c_k \hat{H}_{ik}^1 = E_j \sum_{k \neq j} c_k \langle i|k\rangle$$

$$0 \quad \hat{H}_{ij}^1 + c_i E_i^0 + \sum_{k \neq j} c_k \hat{H}_{ik}^1 = c_i E_j$$

To first order in energy,  $\hat{H}_{ij}^1 + c_i E_i^0 = c_i E_j^0 \Rightarrow c_k = \frac{\hat{H}_{kj}^1}{E_j^0 - E_k^0}$

$$E_j = E_j^0 + \hat{H}_{jj}^1 + \sum_{k \neq j} \frac{\hat{H}_{jk}^1 \hat{H}_{kj}^1}{E_j^0 - E_k^0}$$

# Perturbation Theory – Example of H spin states

$$\hat{H}^0 = \omega_e \hat{S}_z - \omega_p \hat{I}_z + \omega_0 \hat{S}_z \hat{I}_z$$

$$\hat{H}^1 = \frac{1}{2} \omega_0 (\hat{S}_+ \hat{I}_- + \hat{S}_- \hat{I}_+)$$

0 <sup>th</sup> order:	$E_1^0 = \hat{H}_{11}^0 = \frac{1}{2} \omega_e - \frac{1}{2} \omega_p + \frac{1}{4} \omega_0$	$ 1\rangle^0 =  \alpha\alpha\rangle$	1 <sup>st</sup> order:	$\hat{H}_{11}^1 = 0$
	$E_2^0 = \hat{H}_{22}^0 = \frac{1}{2} \omega_e + \frac{1}{2} \omega_p - \frac{1}{4} \omega_0$	$ 2\rangle^0 =  \alpha\beta\rangle$		$\hat{H}_{22}^1 = 0$
	$E_3^0 = \hat{H}_{33}^0 = -\frac{1}{2} \omega_e - \frac{1}{2} \omega_p - \frac{1}{4} \omega_0$	$ 3\rangle^0 =  \beta\alpha\rangle$		$\hat{H}_{33}^1 = 0$
	$E_4^0 = \hat{H}_{44}^0 = -\frac{1}{2} \omega_e + \frac{1}{2} \omega_p + \frac{1}{4} \omega_0$	$ 4\rangle^0 =  \beta\beta\rangle$		$\hat{H}_{44}^1 = 0$

2<sup>nd</sup> order:  $\hat{H}_{12}^1 = 0, \hat{H}_{13}^1 = 0, \hat{H}_{14}^1 = 0, \hat{H}_{24}^1 = 0, \hat{H}_{34}^1 = 0, \hat{H}_{23}^1 = \frac{1}{2} \omega_0$   
 $\hat{H}_{21}^1 = 0, \hat{H}_{31}^1 = 0, \hat{H}_{41}^1 = 0, \hat{H}_{42}^1 = 0, \hat{H}_{43}^1 = 0, \hat{H}_{32}^1 = \frac{1}{2} \omega_0$

$$E_2^0 - E_3^0 = \omega_e + \omega_p - \frac{1}{2} \omega_0 \quad E_3^0 - E_2^0 = -\omega_e - \omega_p + \frac{1}{2} \omega_0$$

Perturbation:  $E_2 = \frac{1}{2} \omega_e + \frac{1}{2} \omega_p - \frac{1}{4} \omega_0 + \frac{\frac{1}{4} \omega_0^2}{\omega_e + \omega_p - \frac{1}{2} \omega_0}$  to 2<sup>nd</sup> order

Exact:  $E_2 \rightarrow \frac{1}{2} \omega_e + \frac{1}{2} \omega_p - \frac{1}{4} \omega_0 + \frac{\frac{1}{4} \omega_0^2}{\omega_e + \omega_p}$  for  $\omega_0^2 \ll (\omega_e + \omega_p)^2$  high field



# The Particle in a Box with Slanted Bottom

a simple example of perturbation theory

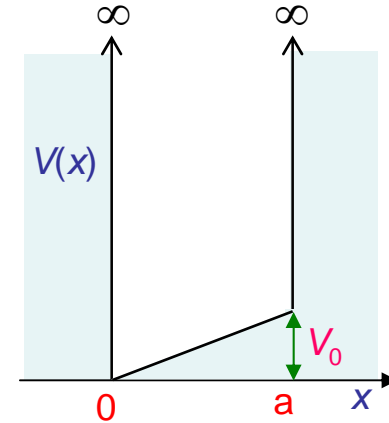
$$\hat{H} = \hat{H}_0 + \hat{h}$$

$$= -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x)$$

$$\hat{h} = V_0 \frac{x}{a}$$

$$V(x) = \infty \quad 0 > x \quad x > a$$

$$V(x) = V_0 \frac{x}{a} \quad 0 \leq x \leq a$$



$$E_n^0 = \frac{n^2 \pi^2 \hbar^2}{2ma^2}$$

$$\psi_n^0 = \left(\frac{2}{a}\right)^{1/2} \sin\left(\frac{n\pi x}{a}\right)$$

$$E_n^{(1)} = \langle \psi_n^0 | \hat{h} | \psi_n^0 \rangle = \frac{V_0}{a} \int_0^a x (\psi_n^0)^* \psi_n^0 dx = \frac{2V_0}{a^2} \int_0^a x \sin^2\left(\frac{n\pi x}{a}\right) dx = \frac{1}{2} V_0$$

⇒ To first order, all energy levels are simply raised by  $\frac{1}{2}V_0$

What if the perturbation was level ( $V_0$ ) across the bottom of the well?

In this case  $E_n^{(1)} = \langle \psi_n^0 | V_0 | \psi_n^0 \rangle = V_0 \langle \psi_n^0 | \psi_n^0 \rangle = V_0$  i.e. all energy levels raised by  $V_0$

and the second-order corrections are zero. The wave functions are unperturbed.

The choice of zero level for potential energy is arbitrary.

# The Born-Oppenheimer Approximation

$$\hat{H}_{\text{TOT}} = -\frac{1}{2} \sum_i \nabla_i^2 - \frac{1}{2} \sum_k \frac{m}{M_k} \nabla_k^2 - \sum_i \sum_k \frac{Z_k}{r_{ik}} + \sum_i \sum_{j>i} \frac{1}{r_{ij}} + \sum_{k_1} \sum_{k_2>k_1} \frac{Z_{k_1} Z_{k_2}}{r_{k_1 k_2}} = \hat{T}_e + \hat{T}_N + V_{eN} + V_{ee} + V_{NN}$$

electrons
nuclei
el-nucl. pairs
electron pairs
pairs of nuclei

For a given molecular geometry, the nuclear coordinates have fixed values ( $R$ ).

Then, for electrons  $[\hat{T}_e + V_{eN} + V_{ee}] \psi_e(R, r) = E_e(R) \psi_e(R, r)$

$E_e(R)$  defines the potential energy surface for motion of the nuclei.

For the nuclei  $[\hat{T}_N + V_{NN} + E_e(R)] \psi_N(R) = \mathcal{E} \psi_N(R)$        $\psi_N(R) =$  the vibrational wave function

For the whole molecule  $\hat{H}_{\text{TOT}} \chi(R, r) = E_{\text{TOT}} \chi(R, r)$

Assume  $\chi(R, r) = \psi_e(R, r) \psi_N(R)$

Then from  $[\hat{T}_e + V_{eN} + V_{ee}] \psi_e(R, r) \psi_N(R) = E_e(R) \psi_e(R, r) \psi_N(R)$

$$\hat{H}_{\text{TOT}} \psi_e(R, r) \psi_N(R) = [\hat{T}_N + V_{NN} + E_e(R)] \psi_e(R, r) \psi_N(R) = E_{\text{TOT}} \psi_e(R, r) \psi_N(R)$$

Compare with  $\psi_e(R, r) [\hat{T}_N + V_{NN} + E_e(R)] \psi_N(R) = \mathcal{E} \psi_e(R, r) \psi_N(R)$

# The Born-Oppenheimer Approximation (cont.)

The eigenvalue  $\mathcal{E}$  is an approximation to the total molecular energy  $E_{\text{TOT}}$ .

It can be identified with  $E_{\text{TOT}}$  under the condition that

$$\begin{aligned}\psi_e(R, r) \hat{T}_N \psi_N(R) &= \hat{T}_N \psi_e(R, r) \psi_N(R) \\ &= -\frac{1}{2} \sum_k \frac{m}{M_k} \nabla_k^2 \psi_e(R, r) \psi_N(R)\end{aligned}$$

But

$$\begin{aligned}\nabla_k^2 \psi_e(R, r) \psi_N(R) &= \frac{\partial}{\partial q_k} \left\{ \psi_e \frac{\partial \psi_N}{\partial q_k} + \psi_N \frac{\partial \psi_e}{\partial q_k} \right\} \\ &= \psi_e \frac{\partial^2 \psi_N}{\partial q_k^2} + \underbrace{\frac{\partial \psi_e}{\partial q_k} \frac{\partial \psi_N}{\partial q_k} + \frac{\partial \psi_N}{\partial q_k} \frac{\partial \psi_e}{\partial q_k}}_{\text{negligible}} + \psi_N \frac{\partial^2 \psi_e}{\partial q_k^2}\end{aligned}$$

If these terms are negligible,  
the condition is satisfied.

The Born-Oppenheimer approximation holds provided  $\frac{\partial \psi_e}{\partial q_k} \approx 0$

i.e. if  $\psi_e$  is a slowly varying function of the nuclear coordinates.