BORN - OPPENHEIMER APPROXIMATION

- FIXED IONS APPROX
- BO - APPROX

- HOW TO SEPARATE ELECTRONIC AND IONIC DEGREES OF FREEDOM

- LARGE MASS DIFFERENCE WILL ALLOW US TO DECOUPLE EQS. FOR IONS / ELECTRONS

WORST CASE HYDROGE $\bigcirc \gg \circ$ 1800 TIMES

URANIUM $235 \times 1800 \gg 1$!

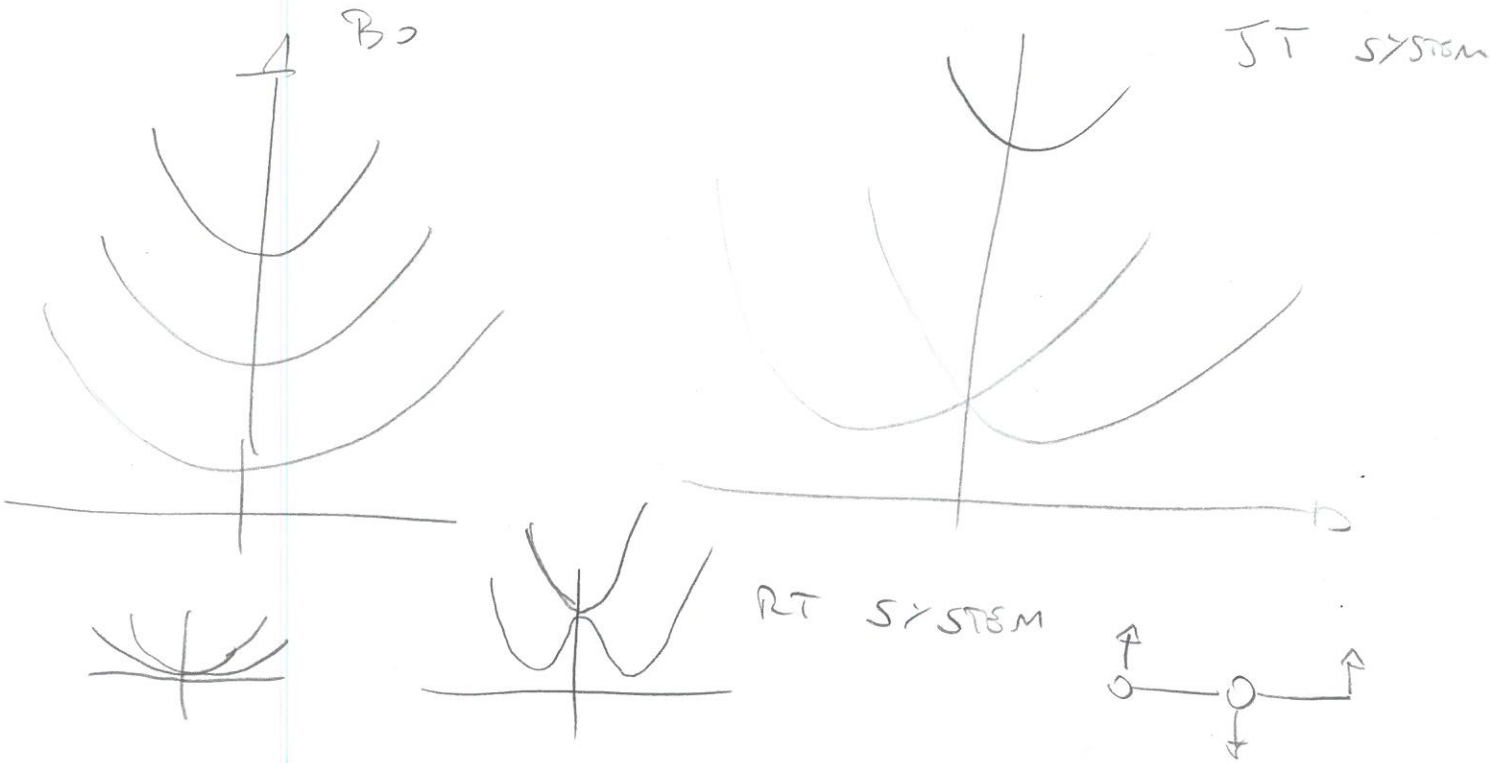
- ORDINARY BO SYSTEM

NON-DEGENERATE GROUND STATE IN THE ZONE OF INTEREST

- NOT ORDINARY BO SYSTEM

TWO OR MORE POTENTIAL SURFACES ARE DEGENERATE

- JAHN-TELLER NON VANISH SPATIAL GRADIENTS
- RENNER-TELLER SYSTEM



◦) FIXED IONS APPROXIMATION

$$H_{TOT} = T_N + T_e + V_{ee} + V_{e\text{-}N} + V_{NN}$$

$$= -\sum_I \frac{\hbar \nabla_I^2}{2M_I} - \sum_i \frac{\hbar_i \nabla_i^2}{2m_i} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - R_j|}$$

$$+ \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J e^2}{|R_I - R_J|} - \sum_{i,I} \frac{Z_I e^2}{|r_i - R_I|^2}$$

$$H_{TOT} = T_N(R) + T_e(r) + V(r, R) \qquad R = 3N \text{ COORDIN}$$

$r = 3n + \text{SPIN}$

FULL SOLUTION

$$[T_N + T_e + V(r, R)]\Psi(r, R) = W \Psi(r, R)$$

VIBRONIC ENERGIES ← W

VIBRONIC WF ← $\Psi(r, R)$

WE SEND $M \to \infty$

$T_N \to 0$

$$[T_e + V(r, R)] \Psi(r, R) = W \Psi(r, R)$$

ERRORS WE MAKE

$$\Psi(r,R) \simeq \Phi(r-R) \qquad [\text{PRODUCT OF } \Phi(r-R) \text{ WF}]$$

SO $\nabla_R = \nabla_r$ THIS MEANS $\nabla_I^2 = \nabla_i^2$

$$T_N = -\frac{\nabla_I^2}{M_I} = -\frac{\nabla_i^2}{M_I}\frac{m_i}{m_i} = -\frac{m_i}{M_I} T_e$$

$$T_N \simeq 10^{-3} T_e \quad !!$$

b) IN THIS APPROXIMATION WE DEFINE

$$H_e(r,R) = T_e + V(r,R)$$

R IS A SIMPLE PARAMETER

$$H_e \Psi(r,R) = E(R)\Psi(r,R)$$

AS WE VARY R WE DEFINE AN ADIABATIC SURFACE

$$M_I \ddot{R} = -\frac{\partial E(R)}{\partial R_I}$$

IONS DYNAMICS

$$E(R) = E(R_0) + \frac{1}{2}\sum_{I,J}\left(\frac{\partial^2 E_0}{\partial R_I \partial R_J}\right)\Delta R_I \Delta R_J + O(\Delta R^3)$$

$$M_I \ddot{\Delta R}_I = -\sum_J \left(\frac{\partial^2 E(R)}{\partial R_I \partial R_J}\right)\Delta R_J$$

WE ASSUME TIME PERIODIC DISPLACEMENTS

$$U_I(t) = A_I e^{-i\omega t}$$

$$-\omega^2 M_I A_I = \sum_J \left(\frac{\partial E}{\partial R_I \partial R_J}\right) A_J$$

PHONONS

BO APPROXIMATION

MAY WE SEPARATE ELECTRON AND IONS WITHOUT M-D ∞ ?

$$H_{TOT}\ \Psi(r,R) = W\Psi(r,R)$$

WF FACTORIZATION

$$\Psi_{TRIAL}(r,R) \cong \chi(R)\,\psi_0(r,R) \qquad (1)$$

ψ_0 ↑ SOLUTION OF THE ELECTRONIC HAMILTONIAN

$$[T_e + V(r,R)]\,\psi_0 = E_0(R)\,\psi_0$$

$\chi(R)$ CAN BE FOUND BY VARIATIONAL PRINCIPLES

$\psi_{0/e}(r,R)$ DEFINE GROUND / EXCITED STATES CONTINUOUS FUNCTION OF R

CHOICE (1) IS NOT UNIQUE BECAUSE

$$\tilde{\psi}(r;R) = e^{i\alpha(R)}\,\psi_0(r;R)$$ GAUGE FREEDOM

— CHOOSE A ψ_0

$$\{T_e + V_e + V_{eI} + V_{II} + T_{eN}\}\,\chi\psi_0 =$$

$$E_0(R)\,\chi\psi_0(r,R) + V_{II}\,\chi\psi_0 + T_N[\chi\psi_0] = W\chi\psi_0$$

$$E_0(R)\chi\psi - \left(\frac{\hbar^2}{2M}\nabla^2\chi(R)\right)\psi_0(r,R) - \frac{\hbar^2}{M}\frac{\partial\chi}{\partial R}\frac{\partial\psi}{\partial R}$$

$$-\chi\frac{\hbar^2}{2M}\frac{\partial^2}{\partial R^2}\psi(r,R) = W\chi\psi$$

$$\left[-\frac{\hbar^2\partial^2}{2M\partial R^2} + E_0(R)\right]\chi(R) + \Lambda_{00}(R)\chi(R) = W\chi(R)$$

$$\Lambda_{00}(R) = \underbrace{-\frac{\hbar^2}{2M}\left\langle\psi_0(r,R)\left|\frac{\partial^2\psi_0(r,R)}{\partial R^2}\right.\right\rangle}_{(A)} \underbrace{-\frac{\hbar^2}{M}\left\langle\psi_0(r,R)\left|\frac{\partial\psi_0}{\partial R}\right.\right\rangle\frac{\partial}{\partial R}}_{(B)}$$

↑ THE "NON-ADIABATIC OPERATOR"

GAUGE DEPENDENT POTENTIAL !

Λ_{00} GARANTEES THAT THE FINAL WF AND ENERGIES ARE GAUGE FREE

(A) IS A CORRECTION TO THE KINETIC ENERGY THAT WE SAW IS OF ORDER m/M

(B) WITHOUT MAGNETIC FIELDS (TIME-INDEPENDENT) $\psi_0(R)$ CAN BE CHOOSEN REAL. IN THIS CASE

$$\left\langle\psi_0\left|\frac{\partial}{\partial R}\right|\psi_0\right\rangle = \int\psi^*\frac{\partial}{\partial R}\psi = \int\psi\frac{\partial}{\partial R}\psi = \frac{1}{2}\frac{\partial}{\partial R}\int\psi\psi = 0$$

DUE TO THE NORMALIZATION OF THE WF

$\left\langle\psi_0\left|\frac{\partial}{\partial R}\right|\psi_0\right\rangle$ IS A GEOMETRIC BERRY CONNECTION !

TWO EQUATIONS

$$\begin{cases} \left[T_e + V(r,R) \right] \psi_0 = E_0(R)\, \psi_0(r;R) \\ \left[-\frac{\hbar^2}{2M} \frac{\partial^2}{\partial R^2} + E_0(R) \right] \chi(R) = W \chi(R) \end{cases}$$

THIS PROCEDURE DOES NOT WORK IN A DEGENERATE CASE ! WE CANNOT FIX WF PHASES

EXACT VIBRONIC WF ARE LINEAR COMBINATION

$$\psi = \sum_i \chi_i(R)\, \psi_i(r,R)$$

IF SURFACES ARE FAR AWAY THIS IS A GOOD APPROX.

ONE DIMENSIONAL EXAMPLE

-) CONSIDER A SINGLE VIBRATIONAL MODE NON-DEGENERATE

$$E_0(R) = E_0(R_0) + \frac{1}{2} c \left(R - R_0\right)^2$$

$$\psi_0(r;R) \simeq \chi_m(R)\, \psi_0(r;R)$$

$\chi_m(R)$ IS A SOLUTION OF THE EQ.

$$\left[-\frac{\hbar^2}{2M} \frac{\partial^2}{\partial R^2} + E_0(R_0) + \frac{1}{2} c \left(R - R_0\right)^2 \right] \chi_m(R) = W_m \chi_m$$

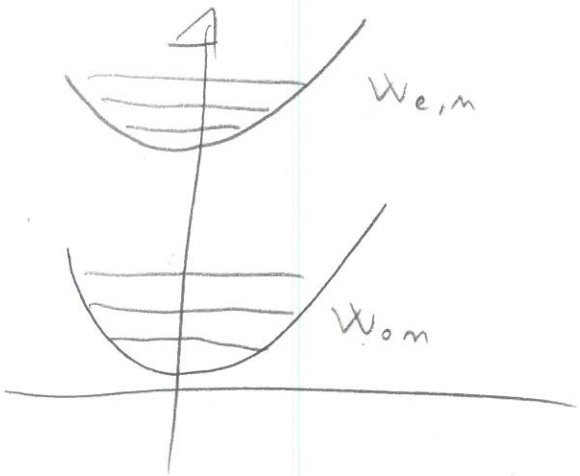
$$W_{gm} = E_0(R_0) + \left(m + \frac{1}{2}\right)\hbar\omega$$

$$\omega = \sqrt{\frac{c}{M}} \qquad m = 0, 1, 2, 3$$

·) CONSIDER NOW AN EXCITED STATE $E_e(R)$

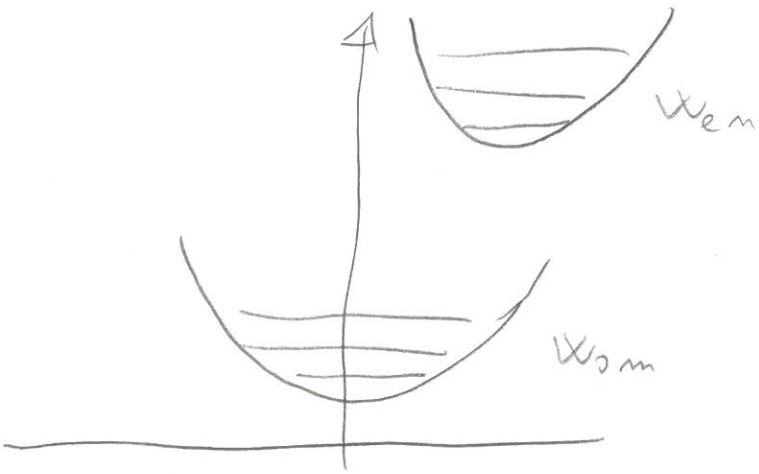
$$\Psi_e(r; R) = \chi_n(R)\,\psi_e(r; R)$$

$$W_{em} = E_e(R_0) + \left(n + \frac{1}{2}\right)\hbar\hat{\omega} \qquad n = 0, 1 \ldots$$



DELOCALIZED ELECTRONS

VALENCE / COND STATES



LOCALIZED ELECTRONS

FRANCK – CONDON

SEITZ-MODEL

SHIFT BETWEEN

ABSORPTION – EMISSION

(MOLECULES
DEFECTS)