MOLECULES

DIATOMIC MOLECULE : 2 NUCLEI
N ELECTRONS

$$H = \underbrace{-\frac{\hbar^2}{2M_a}\Delta_a - \frac{\hbar^2}{2M_b}\Delta_b}_{\text{KINETIC ENERGY OF NUCLEI}} - \underbrace{\frac{\hbar^2}{2m}\sum_{i=1}^{N}}_{\text{KINETIC ENERGY OF N } \bar{e}} + \hat{V}$$

$\hat{V}$ ↑ POTENTIAL ELECTROSTATIC INTERACTIONS BETWEEN ALL PARTICLES

IN THE CENTER OF MASS COORDINATES

$\vec{R} = \vec{R}_a - \vec{R}_b$ POSITION OF NUCLEI (DISTANCE BETWEEN THEM = $|\vec{R}|$)

r_i – RELATIVE POSITIONS OF N $\bar{e}$

$$H = H_0 + H'$$

$$H_0 = -\frac{\hbar^2}{2m}\sum_{i=1}^{N}\Delta_{r_i} + \hat{V}$$

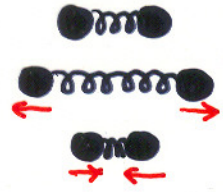
ENERGY OPERATOR OF N $\bar{e}$ IN A MOLECULE WITH INFINITELY HEAVY NUCLEI

$$H' = -\frac{\hbar^2}{2\mu}\Delta_R \quad , \quad \mu^{-1} = M_a^{-1} + M_b^{-1} \quad , \quad \text{IF } M_a = M_b \Rightarrow \infty \quad H' = 0$$

KINETIC ENERGY CAUSED BY CHANGES OF $\bar{R}$: ITS LENGTH → ROTATIONS
ITS DIRECTION → VIBRATION

CENTER OF GRAVITY

ROTATIONAL MOTION



VIBRATIONAL MOTION

TERMS RESPONSIBLE FOR COUPLING BETWEEN MOTION OF NUCLEI AND ELECTRONS (PARTIAL DERNATIVES) ARE NEGLECTED IN H'.

FOR N ELECTRONS IN DIATOMIC MOLECULE WITH INFINITELY HEAVY NUCLEI:

$$H_0 \Psi_k(\bar{r}_1, \bar{r}_2, \ldots \bar{r}_N; \bar{R}) = E_k^0(R)\, \Psi_k(1,2,\ldots N; \bar{R})$$

SOLUTIONS ARE KNOWN

PARAMETRIC DEPENDENCE

FOR GIVEN (FIXED) POSITIONS OF NUCLEI

IF: $H\Psi = E\Psi$; $H = H_0 + H'$ $\Rightarrow$ $\Psi =$ PRODUCT OF APPROPRIATE FUNCTIONS

ASSUMPTION:

$$\Psi = \sum_m \psi_m(\bar{r}_1, \bar{r}_2, \ldots \bar{r}_N; \bar{R})\, f_m(\bar{R})$$

$\Downarrow$ COMPLEX COUPLED DIFFERENTIAL EQUATIONS FOR $f_m(\bar{R})$

SIMPLIFICATION:

$$\Psi = \psi_k(\bar{r}_1, \ldots \bar{r}_N; \bar{R})\, f_k(\bar{R})$$

UNKNOWN FUNCTION (ONE TERM)

„MOTION OF $\bar{e}$ IS ADJUSTED TO SLOW CHANGES OF R"

$$(H_0 + H')\Psi = E\Psi$$

$$(H_0 + H')\psi_k(\bar{r}_1, \ldots \bar{r}_N; \bar{R}) f_k(\bar{R}) = E\,\psi_k(\bar{r}_1, \ldots \bar{r}_N; \bar{R}) f_k(\bar{R})$$

$\int_{d^3\tau_i} \psi_k$

$$\langle \psi_k | H_0 | \psi_k \rangle f_k(\bar{R}) + \langle \psi_k | -\frac{\hbar^2}{2\mu}\Delta_{\bar{R}} | \psi_k \rangle = E f_k(\bar{R}) \langle \psi_k | \psi_k \rangle$$

E_k^0

$$\nabla_{\bar{R}}\nabla_{\bar{R}}(\psi_k f_k) = \nabla_{\bar{R}}(\nabla_{\bar{R}}\psi_k) f_k + \nabla_{\bar{R}}(\nabla_{\bar{R}} f_k)\psi_k =$$

$$= (\nabla_{\bar{R}}\overset{1^0}{\nabla_{\bar{R}}}\psi_k) f_k + (\nabla_{\bar{R}}\psi_k)(\nabla_{\bar{R}} f_k) + (\nabla_{\bar{R}}\psi_k)(\nabla_{\bar{R}} f_k) + (\overset{2^0}{\nabla_{\bar{R}}\nabla_{\bar{R}}} f_k)\psi_k$$

$\int \psi_k$

$$\nabla_{\bar{R}}\{\langle \psi_k | \psi_k \rangle = 1\} \Rightarrow \int \psi_k \nabla_{\bar{R}} \psi_k \, d\tau = 0$$

$$\langle \psi_k | \overset{1^0}{\nabla_{\bar{R}}\nabla_{\bar{R}}} | \psi_k \rangle f_k + \langle \psi_k | \psi_k \rangle \overset{2^0}{\nabla_{\bar{R}}\nabla_{\bar{R}}} f_k$$

NEW EQUATION FOR $f_k(\bar{R})$

$$\left[-\frac{\hbar^2}{2\mu}\Delta_{\bar{R}} + E_k^0(R) + H'_{kk}(\bar{R})\right] f_k(\bar{R}) = E f_k(\bar{R})$$

$$\left[-\frac{\hbar^2}{2\mu}\Delta_{\bar{R}} + E_k^0(R) + H'_{kk}(R)\right] f_k(\bar{R}) = E f_k(\bar{R})$$

DESCRIBES MOTION OF NUCLEI

$$H'_{kk}(R) = \langle \psi_k | H' | \psi_k \rangle$$

NEW POTENTIAL

$$U_k(\bar{R}) = E_k^0(\bar{R}) + H'_{kk}(\bar{R})$$

ENERGY OF N ELECTRONS IN THE STATE ψ_k

INFLUENCE OF MOTION OF NUCLEI UPON THE ENERGY OF ELECTRONS

$$H' = -\frac{\hbar^2}{2\mu}\Delta_R$$

SMALL CORRECTION TO THE ENERGY $E_k^0(R)$

$$\frac{1}{\mu} = \frac{1}{M_a} + \frac{1}{M_b}$$

VERY HEAVY NUCLEI

BORN-OPPENHEIMER APPROXIMATION $H'_{kk} = 0$

$$U_k(R) = E_k^0(R)$$

IF H'_{kk} IS TAKEN INTO ACCOUNT

$$U_k(R) = E_k^0(R) + H'_{kk}(R)$$

ADIABATIC APPROXIMATION

THIS IS A CONSEQUENCE OF THE ASSUMPTION

$$\Psi = \psi_k(\bar{r}_1, \ldots \bar{r}_N; \bar{R}) f_k(\bar{R})$$

THE MOST ACCURATE POTENTIAL ENERGY OF THE MOTION OF NUCLEI

IN ORDER TO INCLUDE NON-ADIABATIC EFFECTS

$$\Psi = \sum_m \psi_m(\bar{r}_1, \ldots \bar{r}_N; \bar{R}) f_m(\bar{R})$$

THERE IS NO SEPARATION OF VARIABLES!

NO SEPARATION OF MOTION OF NUCLEI AND ELECTRONS

HOW TO SOLVE EQUATIONS FOR $f_k(\bar{R})$?

$$\left[-\frac{\hbar^2}{2\mu}\Delta_R + U_k(R)\right] f_k(\vec{R}) = E f_k(\vec{R})$$

$U_k(R) = U_k(|\vec{R}|)$: $\vec{R} = (R, \theta, \varphi)$ SPHERICAL COORDINATES

$$f_k(\vec{R}) = Y(\theta,\varphi)\chi_k(R)\frac{1}{R}$$

SEPARATION OF VARIABLES

$\Delta_{\vec{R}} \Rightarrow \Delta_{R\theta\varphi}$:

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\varphi^2} + \lambda Y = 0 \quad \text{ANGULAR PART}$$

$$-\frac{\hbar^2}{2\mu}\frac{d^2\chi_k}{dR^2} + \left[U_k(R) + \frac{\lambda\hbar^2}{2\mu R^2}\right]\chi_k = E\chi_k \quad \text{RADIAL PART}$$

HYDROGEN ATOM

Y- SPHERICAL HARMONICS

THE SOLUTIONS ARE OF CLASS Q IF $\lambda = J(J+1)$

ROTATIONAL QUANTUM NUMBER

DEFINES THE ANGULAR MOMENTUM OF A MOLECULE

$J = 0, 1, 2, \ldots$

$M = -M, \ldots M$ $(2J+1$ VALUES$)$

RADIAL PART

$$-\frac{\hbar^2}{2\mu}\frac{d^2\chi_{kvJ}}{dR^2} + V_{kJ}(R)\chi_{kvJ} = E_{kvJ}\chi_{kvJ} \quad (**)$$

$$V_{kJ}(R) = U_k(R) + J(J+1)\frac{\hbar^2}{2\mu R^2}$$

ONE-DIMENTIONAL MOTION DUE TO THE CHANGES OF R (= LENGTH = DISTANCE BETWEEN THE NUCLEI)

VIBRATIONAL MOTION WITHIN THE POTENTIAL $V_{kJ}(R)$

$$V_{kJ}(R) = U_k(R) + J(J+1)\frac{\hbar^2}{2\mu R^2}$$

ADIABATIC POTENTIAL — DEPENDS ON THE STATE K OF ALL ELECTRONS

ROTATIONAL TERM — DEPENDS ON THE ROTATIONAL QUANTUM NUMBER J

FOR GIVEN K AND J $\Rightarrow$ VARIOUS SOLUTIONS v OF $(**)$

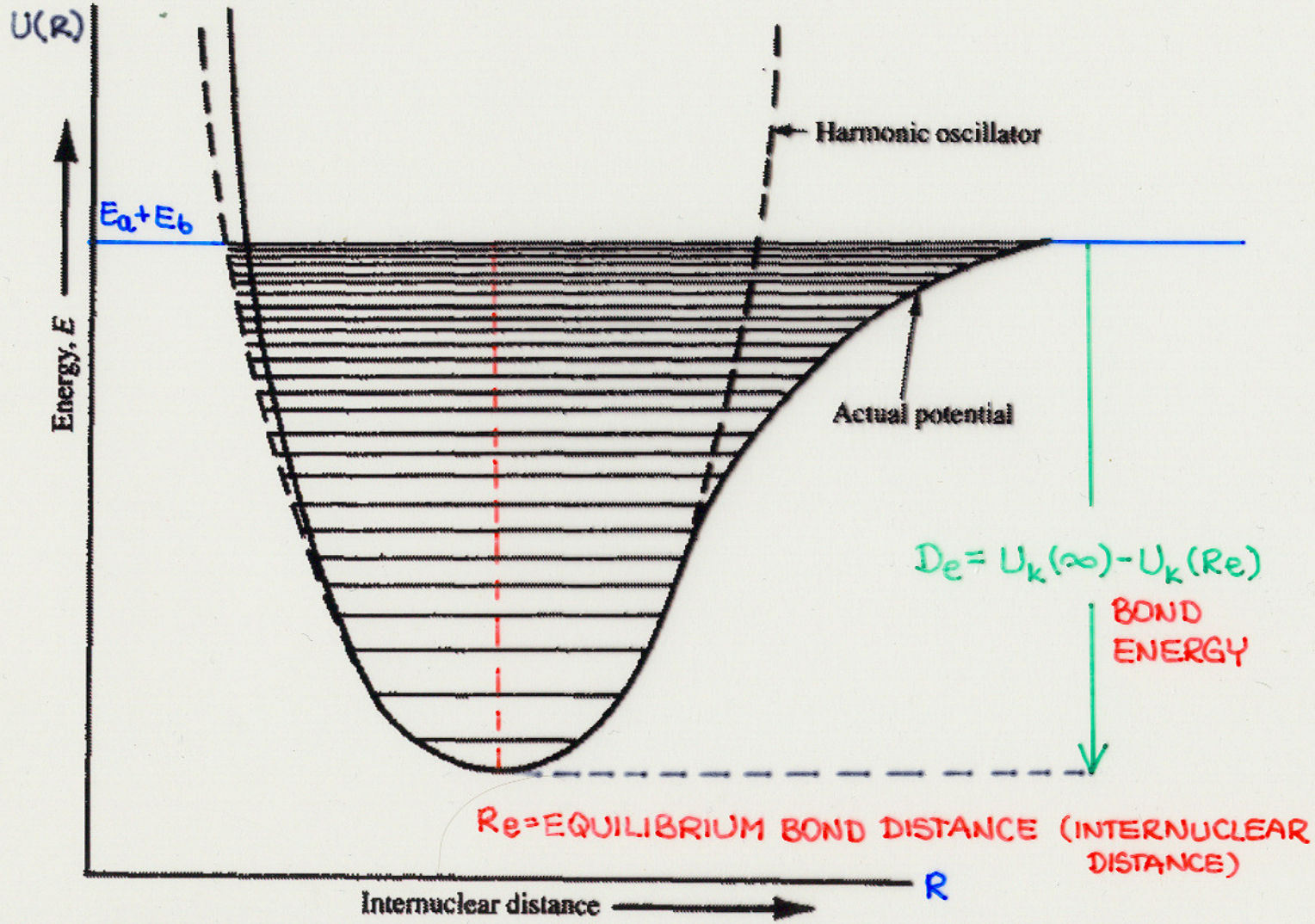


Figure 4-15 Comparison between the actual potential and the harmonic oscillator potential for a diatomic molecule.

$$-\frac{\hbar^2}{2\mu}\frac{d^2\chi_{kvJ}}{dR^2} + \left[U_k(R) + J(J+1)\frac{\hbar^2}{2\mu R^2}\right]\chi_{kvJ} = E_{kvJ}\chi_{kvJ}$$

POTENTIAL

APPROXIMATIONS FOR $U_k(R)$ (ADIABATIC POTENTIAL

$$= E_k^0(R) + H'_{kk}(R)$$

MORSE POTENTIAL

$$U_k(R) = De\left[1 - e^{-a(R-Re)}\right]^2$$

"DEPTH" — WIDTH

EXPANSION: TAYLOR SERIES (AROUND Re)

$$U_k(R) = U_k(Re) + \left(\frac{dU_k}{dR}\right)_{R=Re}(R-Re) + \frac{1}{2}\left(\frac{dU_k}{dR^2}\right)_{R=Re}(R-Re)^2 + \dots$$

$\left(\frac{dU_k}{dR}\right)_{R=Re} = 0$ minimum

$$U_k(R) = U_k(Re) + \frac{1}{2}\mathcal{K}(R-Re)^2$$

$$\mathcal{K} = \left(\frac{d^2U_k}{dR^2}\right)_{R=Re}$$

FORCE CONSTANT

POTENTIAL (APPROXIMATED)

$$V_{kJ}(R) = U_k(Re) + \frac{J(J+1)\hbar^2}{2\mu Re^2} + \frac{1}{2}\mathcal{K}(R-Re)^2$$

INDEPENDENT OF R

ADDITIVE TERMS TO THE TOTAL ENERGY

ASSUMPTION

$$\frac{J(J+1)\hbar^2}{2\mu R^2} \simeq \frac{J(J+1)\hbar^2}{2\mu Re^2}$$

FINAL EQUATION FOR χ:

HARMONIC OSCILLATOR!

$$-\frac{\hbar^2}{2\mu}\frac{d^2\chi_{kvJ}}{dR^2} + \frac{1}{2}\mathcal{K}(R-Re)^2\chi_{kvJ} = E'\chi_{kvJ}$$

$$E' = E_{kvJ} - U_k(Re) - \frac{J(J+1)\hbar^2}{2\mu Re^2}$$

VIBRATIONAL ENERGY — TOTAL ENERGY — ELECTRONIC ENERGY — ROTATIONAL ENERGY

FOR HARMONIC OSCILLATOR

$$E' = h\nu_0\left(\nu + \tfrac{1}{2}\right)$$

ν ← VIBRATIONAL QUANTUM NUMBER

TOTAL ENERGY OF A MOLECULE

$$E_{k\nu J} = U_k(Re) + h\nu_0\left(\nu + \tfrac{1}{2}\right) + \frac{J(J+1)\hbar^2}{2\mu Re^2}$$

$E_{TOTAL} = E_{ELECTRONIC} + E_{VIBRATIONAL} + E_{ROTATIONAL}$

$E_{ELECTRONIC}$: k; $E_{VIBRATIONAL}$: ν; $E_{ROTATIONAL}$: J

THE LOWEST ENERGY: $k = 0$ (GROUND STATE), $\nu = 0$, $J = 0$

$$E_{000} = U_0(Re) + \tfrac{1}{2} h\nu_0$$

DUE TO OSCILLATIONS IT IS IMPOSSIBLE TO REACH THE ENERGY $U_0(Re)$ WHICH IS THE MINIMUM OF THE POTENTIAL

$$D_0 = U_0(\infty) - E_{000}$$

DISSOCIATION ENERGY

SEPARATE ATOMS IN THE GROUND STATES

THE LOWEST ENERGY STATE OF A MOLECULE

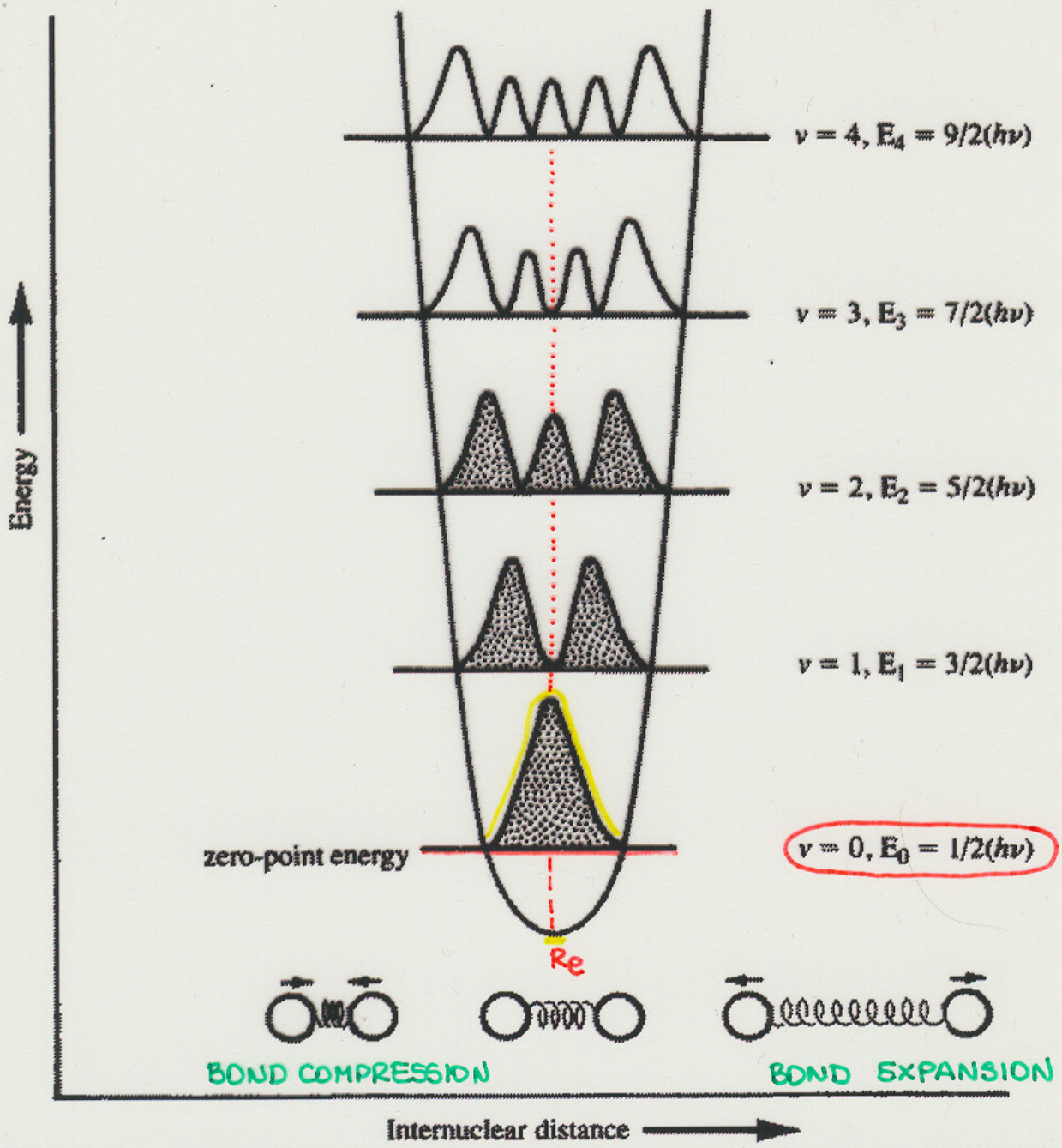


Figure 4-14 Potential energy curve for a diatomic molecule assuming that its vibrational motion can be described as a harmonic oscillator. The shaded region on each vibrational energy level represents the probability distribution of the vibrational wave function.

1. ENERGY LEVELS ARE EVENLY SPACED (HARMONIC APPROXIMATION)
2. ZERO-POINT ENERGY $E_0 = \frac{1}{2} h\nu_0$
3. LARGE PROBABILITY TO FIND THE MOLECULE AT THE EQUILIBRIUM INTERNUCLEAR DISTANCE IN THE LOWEST VIBRATIONAL STATE $v=0$; FOR HIGHER STATES PROBABILITY IS LARGER AT THE EXTREMES OF BOND COMPRESSION AND EXPANSION