

Potential Energy Surfaces - Force fields

Lecture 3

CHM 624

Molecular Simulations

Varadharajan Srinivasan
Dept. Of Chemistry
IISER Bhopal

Outline

- Breaking up the potential energy surface - force fields
- Bond stretch
- Bond angles
- Torsions
- Non-bonded interactions

$$\rightarrow i\hbar \frac{\partial}{\partial t} \chi_0(\vec{R}, t) = \left[-\hbar^2 \sum_I \frac{\nabla_I^2}{M_I} + U(\vec{R}) \right] \chi_0(\vec{R}, t) \quad \text{--- (1)}$$

$$U(\vec{R}) = E_0(\vec{R}) + \frac{1}{4\pi\epsilon_0} \sum_{I, J} \frac{Z_I Z_J}{|\vec{R}_I - \vec{R}_J|} \quad \text{--- (2)}$$

\downarrow
 electronic ground state energy

ground state PES.

$$\hat{H}_u(\vec{R}) \Psi_n(\vec{r}; \vec{R}) = E_n(\vec{R}) \Psi_n(\vec{r}; \vec{R}) \quad \text{--- (3)}$$

$$\therefore M_I \gg m_e$$

$$M_I \frac{d^2 \vec{R}_I}{dt^2} = - \nabla_I U(\vec{R}) \quad \text{--- (4)''}$$

In order to determine equilibrium properties of any (molecular) system it is enough to know the set of positions & momenta of all constituent atoms at any given time.

$$Q \equiv Q \left(\{ \vec{R}_i, \vec{p}_i \}, t \right) \quad \text{--- (5)}$$

2 ways to calculate $U(\vec{R})$:

(1) compute $U(\vec{R})$ on a grid of \vec{R} values
and interpolate/fit to a functional form

$$U \equiv U(\vec{R}_1, \vec{R}_2, \dots, \vec{R}_N)$$

$$\equiv U(q_1, q_2, \dots, q_{3N-6})$$

$Q = \{q_i\} \rightarrow$ internal coordinates

bond lengths, bond angles,

torsion/dihedral angle

$3N-6$
10
grid pts

(2) Compute $V(\vec{R})$ "on-the-fly" along
some trajectory or as and when
needed. Car-Parrinello Method.

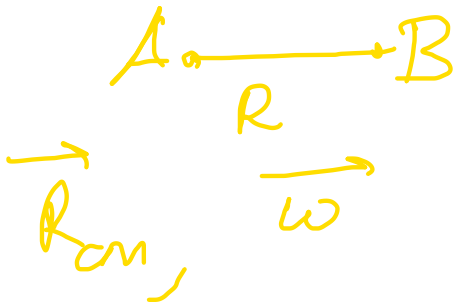
QM calculations are terribly expensive

DFT, HF $\rightarrow O(K^3)$ $K \rightarrow$ no. of
basis functions

CI based
method $\rightarrow O(N^6) - O(N^{10})$ $N \rightarrow$ no. of
electron

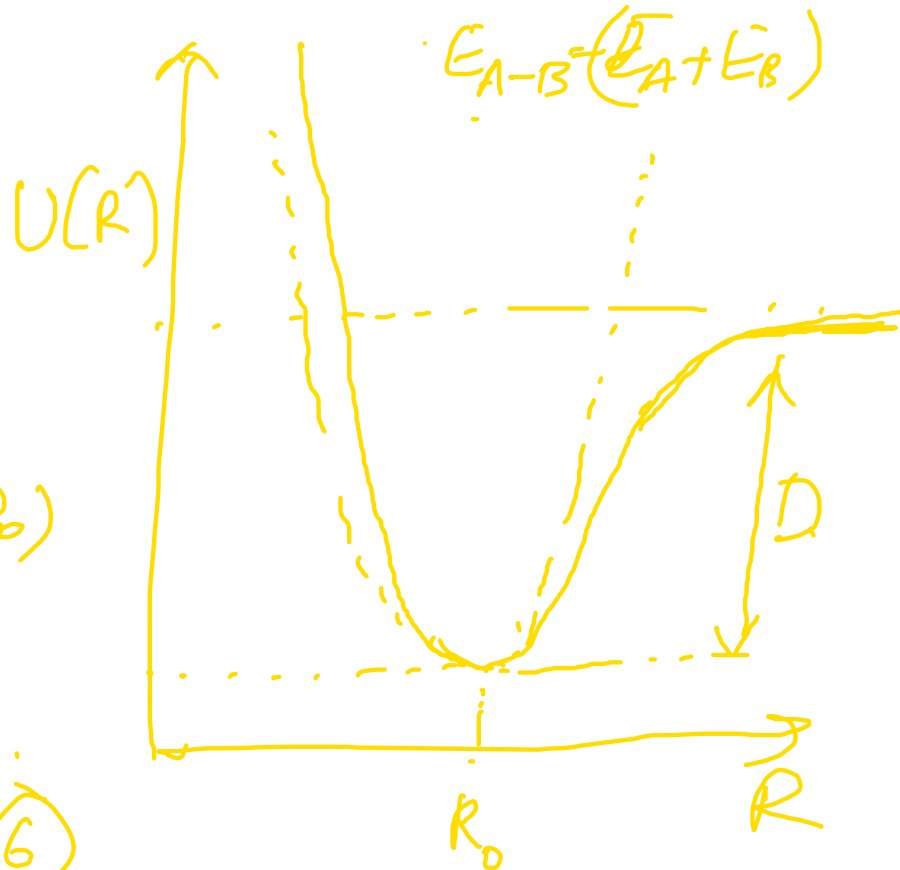
(3) Expressing $U(R)$ in terms of known interaction
 & parametrizing the coupling constants.

Consider a diatomic molecule $\rightarrow A-B$.



$$U(R) \approx U(R_0) + \left. \frac{\partial U}{\partial R} \right|_{R_0} (R - R_0) + \frac{1}{2} \left(\left. \frac{\partial^2 U}{\partial R^2} \right|_{R_0} \right) (R - R_0)^2 + \dots$$

— (6)



→ like simple Harmonic oscillation

$$E(x) = \frac{1}{2} k x^2$$

$$\begin{aligned} & \text{--- } \textcircled{7} \\ x & \rightarrow R \end{aligned}$$

$$U(R) = \frac{1}{2} k (R - R_0)^2$$

$$\begin{aligned} E & \rightarrow U - U(R_0) \\ & \Rightarrow U \end{aligned}$$

$$k = \left(\frac{d^2 U}{dR^2} \right)_{R_0}$$

$\textcircled{8}$

(k, R_0) → 2 parameters

$\textcircled{8}$ → parametric form for $U(R)$

$$\Delta R = |\vec{R}| - |\vec{R}_0| \quad U - U(\vec{R}_0) \implies U(\Delta R) \\ = R - R_0.$$

Morse function:

$$U(\Delta R) = D \left(1 - e^{-\alpha \Delta R} \right)^2 \quad (9)$$

$D \rightarrow$ dissociation energy

$\alpha \rightarrow$ related to k

$$U(\Delta R) \approx D \left[1 - \left(1 - \alpha \Delta R + \frac{1}{2} \alpha^2 \Delta R^2 + \dots \right) \right]^2 \\ = D \alpha^2 \left[1 - \alpha \Delta R + \frac{7}{12} \alpha^2 \Delta R^2 + \dots \right] \Delta R^2 \quad (10)$$

$$\left. \begin{aligned} k &= 2D\alpha^2 \\ \text{or } \alpha &= \sqrt{\frac{k}{2D}} \end{aligned} \right\} \textcircled{11}$$

reduced mass $\leftarrow \mu \omega^2 = k$

In practice, Morse function has very low restoring forces at longer bond lengths \Rightarrow convergence to equilibrium bond lengths will be slow.

For anharmonic effects, a 4th order polynomial is quite adequate.

$$U(\Delta R) = \frac{1}{2} k (\Delta R)^2 \left[1 - \alpha (\Delta R) + \frac{7}{12} \alpha^2 (\Delta R)^2 \right] \quad (11)$$

For most purposes the harmonic form of $U(\Delta R)$ is good enough.

⇒ If there were only bond stretches in the molecule, then

$$U(\Delta R) = \sum_{\langle I, J \rangle} \frac{1}{2} k_{IJ} (R_{IJ} - R_{IJ}^0)^2 \quad (12)$$

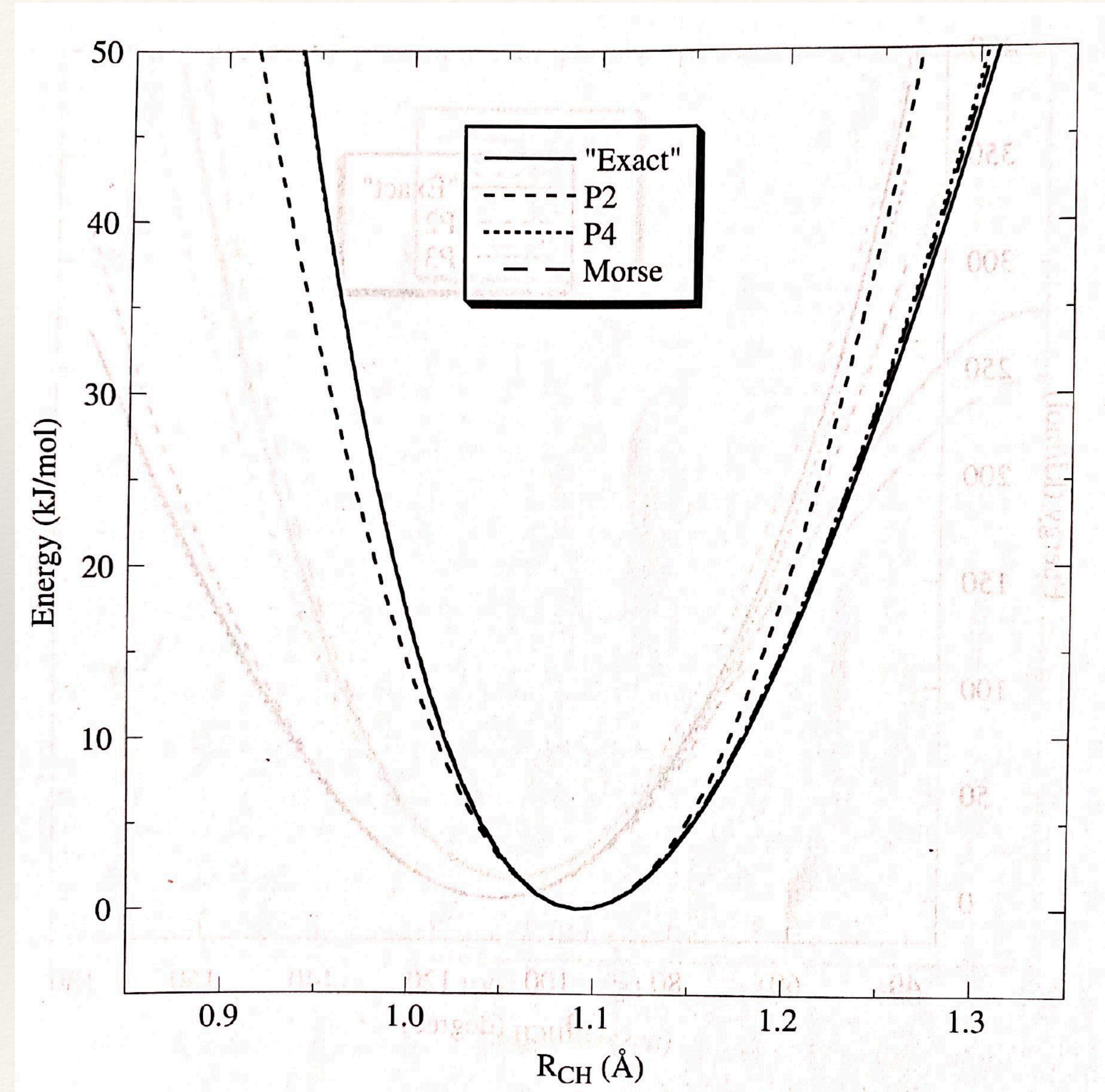
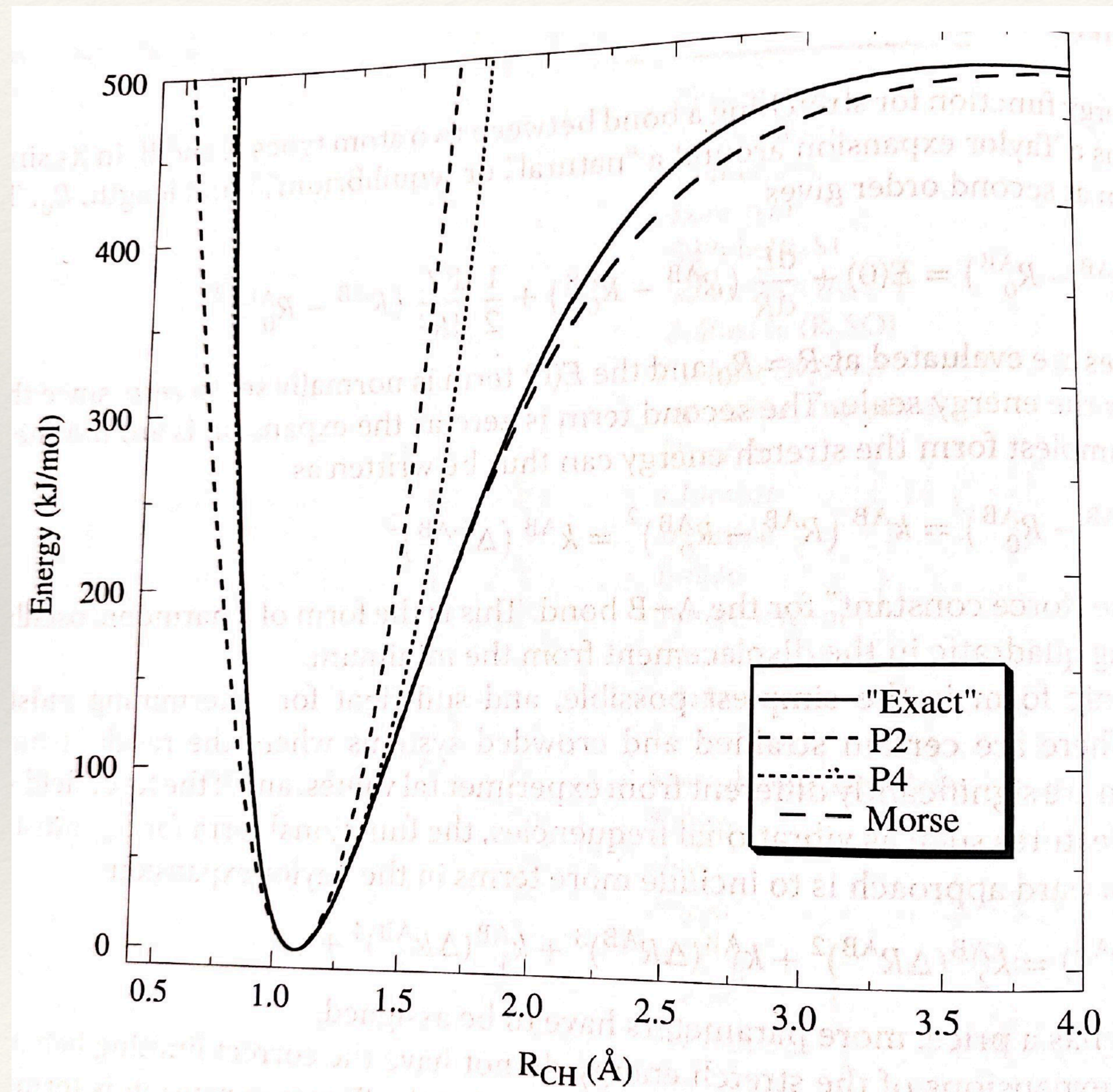
$R_{IJ}^0 \rightarrow$ "natural" bond length

$\langle IJ \rangle \rightarrow$ only bonded pair of atoms I & J

In reality, $U(\vec{R}) = U_{\text{stretch}}(\Delta R) + U_{\text{other}}(\vec{R})$

\Rightarrow an optimization of U in terms of \vec{R} will not necessarily yield $R_{IJ} = R_{IJ}^0$

Bond stretch



Taken from Introduction to Computational Chemistry (F. Jensen)