

# Rational potentials and molecular physics

*From perturbation theory, multipole expansion, tunneling towards  
the theory of diatomic molecules*

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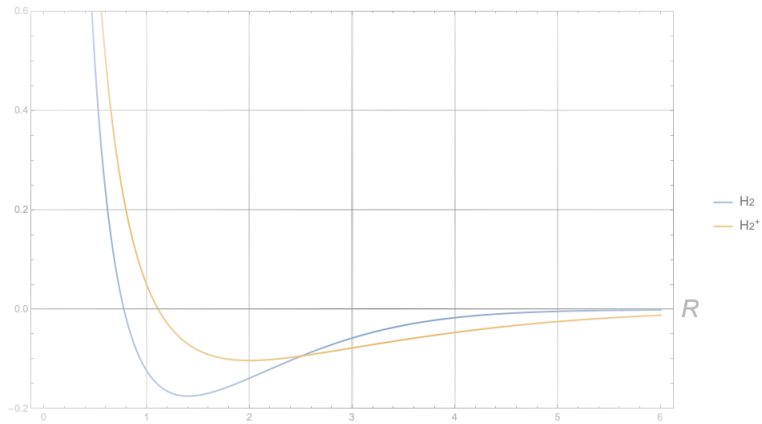
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# Content

- 1 (I) Positively charged heteronuclear molecules  $(A+B)^+$
- 2 (II) Positively charged homonuclear molecular ions  $(A+A)^+$
- 3 Examples:  $H_2^+$  and  $He_2^+$
- 4 Rotational and vibrational states
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## POTENTIAL CURVE - definition

Take  $k$  electrons and two (infinitely) heavy nucleus  $Z_A, Z_B$

- Electronic Hamiltonian

$$\mathcal{H}_e = T_e + V(r_e; R)$$

- Kinetic energy

$$T_e = -\frac{1}{2} \sum_{i=1}^k \nabla_i^2(\mathbf{r}_e) \quad , \quad m_e = 1$$

- Translation-invariant potential

$$V(r_e; R) = \frac{Z_A Z_B}{|\mathbf{R}_1 - \mathbf{R}_2|} + V_{en}(r_{eN}) + V_e(r_{ee})$$

corresponds to  
internuclear interaction, electron-nuclear interaction, electron-electron interactions.

- Nuclei  $Z_{A,B}$  are clamped; they play the role of charged centers

## Bohr-Oppenheimer approximation

- Schrödinger (electronic) equation

$$\mathcal{H}_e \Psi(r) = E(R) \Psi(r)$$

Eigenvalue  $E(R)$  is called the **POTENTIAL CURVE**

$R = |\mathbf{R}_1 - \mathbf{R}_2|$  is classical (non-dynamic) variable, plays a role of *parameter*

This equation is the Subject to the so-called **ab initio** calculations

- two-body Schrödinger (nuclear) equation

$$\left( -\frac{1}{\mu} \Delta_R + E(R) \right) \Psi(R) = E \Psi(R)$$

$\mu$  is reduced mass

## GOAL:

To construct analytical expression for the lowest potential energy curve

**matching** asymptotics at small and large  $R$

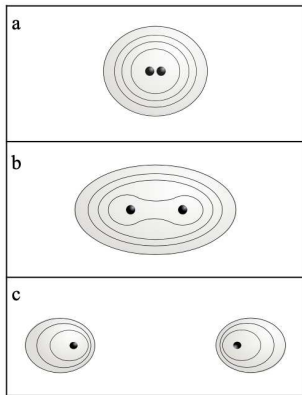
## Physics Idea:

Taking nuclei as probes in electronic media and measuring the screening

$$V(R) = \frac{Z_A Z_B}{R} S(R)$$

(from Coulomb repulsion to van der Waals attraction)

# Electronic Clouds vs $R$



(I) Positively charged heteronuclear molecules  $(A+B)^+$ 

Once positively-charged diatomic molecular ion

- 2 nuclear charges ( $Z_A$  ,  $Z_B$ )
- $(Z_A + Z_B - 1)$  electrons

As a function of the internuclear distance  $R$ , the interaction potential is

- $R \rightarrow 0$ : Perturbation theory

$$V(R) = \frac{Z_A Z_B}{R} + E_a + E_1 R + O(R^2) , \quad (1)$$

$E_1 = 0$  (it is correct for ground state, Buckingham (1958), Bingel (1959))

- $R \rightarrow \infty$ : neutral atom - ion interaction (multipole expansion)

$$V(R) = \frac{C_4}{R^4} + \frac{C_5}{R^5} + \frac{C_6}{R^6} + \dots , \quad (2)$$

$C_5 = 0$  (L. Pauling (1935), Margenau (1931,1971))



Making interpolation between two limits  $R \rightarrow 0$  and  $R \rightarrow \infty$

(matching the expansions (1) and (2) into single function)

$\Rightarrow$  two-point Padé Approximant (definition):

$$P[N/M](R) = \frac{P_N(R)}{Q_M(R)}$$

Explicitly,

$$V(R) = \frac{Z_A Z_B}{R} \frac{P_N(R)}{Q_{N+3}(R)}$$

Meaning:  $P[N/N+3](R) \equiv \frac{P_N(R)}{Q_{N+3}(R)}$  plays a role of (*anti*)-screening of nuclei

$$Q(R) > 0 \text{ for } R > 0$$

(II) Positively charged homonuclear ions (A+A)<sup>+</sup>

As a function of the internuclear distance  $R$  the interaction potential is

- $R \rightarrow 0$  (pert theory)

$$V(R) = \frac{Z^2}{R} + E_a + \underbrace{E_1}_{=0} R + O(R^2) \quad (3)$$

- $R \rightarrow \infty$  (multipole expansion)

$$V(R) = \frac{c_4}{R^4} + \frac{\overbrace{c_5}^{=0}}{R^5} + \frac{c_6}{R^6} + \dots \quad (4)$$

- The problem has additionally *parity*:

(anti)-symmetric under the interchange of nuclei (charges)

Permutational invariance  $\Rightarrow$  Degeneration for  $R \rightarrow \infty$

It implies: Multipole expansions for two lowest states coincide!

**It is double-well potential problem with symmetric Coulomb wells!**

Exponentially-small terms must occur!

- Energy gap  $\Delta E = (E_- - E_+)$ :

*Difference between the first excited ( $E_-$ ) and the ground state ( $E_+$ )*

$$\Delta E = De^{-S_0} \left( 1 + \frac{\delta_1}{R} + \frac{\delta_2}{R^2} + \dots \right)$$

It is like one-instanton expansion in QFT!

$$S_0 = \alpha R \quad , \quad D = C R^\beta$$

Parameters  $\alpha, \beta, \delta_1, \delta_2, \dots$  depend on system

(for all molecules  $\beta$  is integer or half-integer - theoretical mystery!)

- Mean Energy  $E_0$ :

$$E_0 = \frac{E_- + E_+}{2}$$

$E_0$  (mean energy)

- $R \rightarrow 0$

$$E_0^{(0)} = \frac{Z^2}{R} + e_a + e_1 R + O(R^2) \quad (5)$$

- $R \rightarrow \infty$

$$E_0^{(\infty)} = \frac{c_4}{R^4} + \frac{0}{R^5} + \frac{c_6}{R^6} + \dots \quad (6)$$

Interpolation

$$E_0(R) = \frac{1}{R} \text{Pade}[N/N+3](R) \quad (7)$$

(some) Free parameters are set to reproduce  $n_0$  terms in expansion for small and  $n_\infty$  terms for large internuclear distances

$$E_0(R)_{\{n_0, n_\infty\}} = \frac{Z^2}{R} \frac{P_N(R)}{Q_{N+3}(R)} \quad (8)$$

similar to heteronuclear molecular ions!

$\Delta E$  (energy gap)

- $R \rightarrow 0$

$$\Delta E^{(0)} = \varepsilon_{u.a.} + \varepsilon_1 R + O(R^2) \quad (9)$$

- $R \rightarrow \infty$

$$\Delta E_0^{(\infty)} = D e^{-\alpha R} \left( 1 + \frac{\delta_1}{R} + \dots \right) + O(e^{-2\alpha R}) \quad (10)$$

The interpolation depends on the explicit form of  $D \sim R^{k+\tilde{\delta}}!$

$$\Delta E(R)_{\{n_0, n_\infty\}} = (R + \hat{\delta})^{\tilde{\delta}} e^{-\alpha R} \frac{P_{N+k}(R)}{Q_N(R)}$$

$\hat{\delta}$  is parameter,  $\tilde{\delta} = 0$  or  $1/2$ ;  $Q_N(R) > 0$  for  $R > 0$

Eventually,

Potential energy curves

$$E_{\pm}(R) = E_0(R) \mp \frac{1}{2} \Delta E(R)$$

**Examples:  $\text{H}_2^+(p, p, e)$  and  $\text{He}_2^+(\alpha, \alpha, 3e)$**

( $\text{H}_2^+$  is the most studied case theoretically)

$$\text{H}_2^+: \quad E_0 = (E_{1s\sigma_g} + E_{2p\sigma_u})/2$$

- $R \rightarrow 0$

$$E_0 = \frac{2}{R} - \frac{5}{2} + 0 \cdot R + \frac{79}{30}R^2 + \dots$$

- $R \rightarrow \infty$

$$E_0 = -\frac{9}{2R^4} + \frac{0}{R^5} - \frac{15}{R^6} - \frac{213}{2R^7} + \dots$$

- Interpolation with Padé approximant

$$\frac{1}{R} \text{Pade}[5/8](R)$$



$$\text{H}_2^+: \quad \Delta E = E_{2p\sigma_u} - E_{1s\sigma_g}$$

- $R \rightarrow 0$

$$\Delta E = 3 - \frac{27}{5} R^2 + \dots$$

- $R \rightarrow \infty$

$$\Delta E = 8 R e^{-R-1} \left[ 1 + \frac{1}{2R} - \frac{25}{8R^2} - \frac{131}{48R^3} + \dots \right]$$

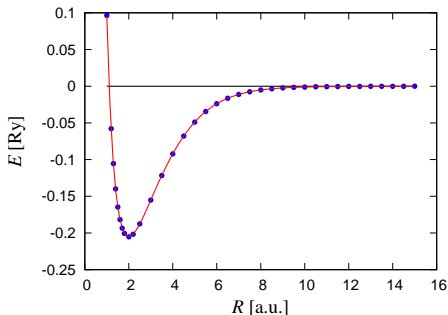
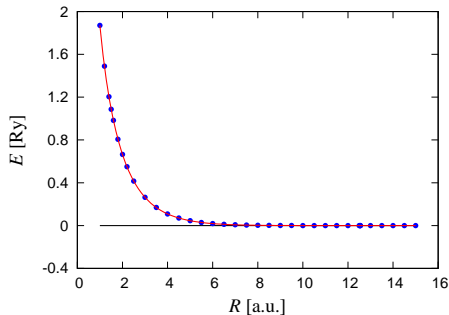
(one-instanton expansion, tunneling between Coulomb wells: J Cizek et al (1986) )

- Interpolation: Padé approximant for  $\Delta E$

$$\left( \text{Pade}[N + 1/N](R) \equiv \frac{P_{N+1}(R)}{Q_N(R)} \right) e^{-R}$$

Potential energy curves are recovered with

$$E_{1s\sigma_g/2p\sigma_u} = E_0 \mp \frac{1}{2}\Delta E$$

●  $1s\sigma_g$ ●  $2p\sigma_u$ 

**4-5 significant digits in energy (for any  $R$ ) in available experimental data are reproduced!**

The analytic curves with 10-11 figures accuracy:

AT + H.Olivares, J Phys B (2011) (highlighted)

Analytic expression for the potential energy curve

⇒ **Rotational and vibrational states**

In the B-O approximation the rovibrational states are calculated by solving the 2-body Schrödinger equation for the nuclear motion

$$\left[ -\frac{1}{\mu} \frac{d^2}{dR^2} + \frac{L(L+1)}{\mu R^2} + V(R) \right] \Phi(R) = E_{\nu L} \Phi(R) \quad (11)$$

where

$$\begin{aligned} \mu &= M_{p,\alpha}/2 \\ V(R) &: \text{Total electronic energy} \\ L &: \text{Total angular momentum} \end{aligned}$$

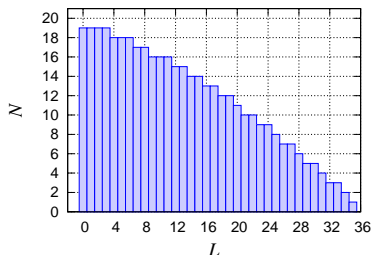
⇒ Lagrange Mesh Method

Procedure for solving the Schrödinger equation by placing it into a non-uniform lattice defined by zeroes of orthogonal polynomials



- $1s\sigma_g$

19 vibrational states ( $L = 0$ )



420 rovibrational states ( $\nu, L$ )

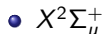
- $2p\sigma_u$

1 vibrational state ( $1, 0$ )

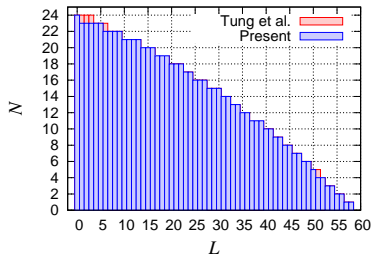
3 rotational states

$$(\nu, L): \quad \begin{array}{l} (0, 0) \\ (0, 1) \\ (0, 2) \end{array}$$

**4-5 significant digits reproduced of experimental or *ab initio* calculations**  
 IT defines DOMAIN OF APPLICABILITY OF B-O APPROXIMATION!



24 vibrational states ( $L = 0$ )



825 rovibrational states ( $\nu, L$ )

3-5 significant digits



3 vibrational states

6 rotational states

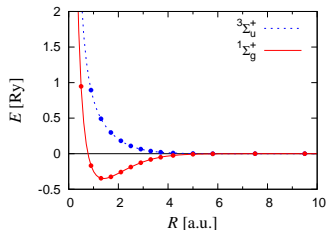
$$(\nu, L): \quad \begin{aligned} \nu &= 0, 1, 2 \\ L &= 0, \dots, 5 \end{aligned}$$

H<sub>2</sub>

The ground and first excited state

$$E(R) = \frac{1}{R} \text{Pade}_1[N/N + 5](R) \pm \frac{1}{2} e^{-2R} \text{Pade}_2[N + 5/N](R^{1/2})$$

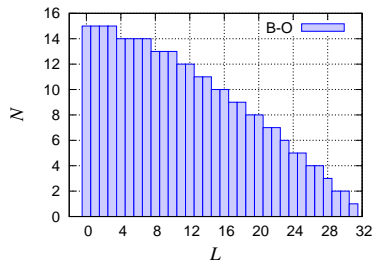
$N = 7 \rightarrow (13+13)$  free parameters (13 + 13 *ab initio* points or exp.data)







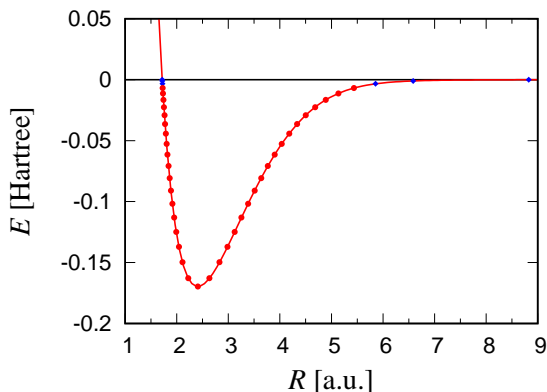
Ground state: 301 rovibrational states



**3-5 significant digits**

in agreement with exp.data!

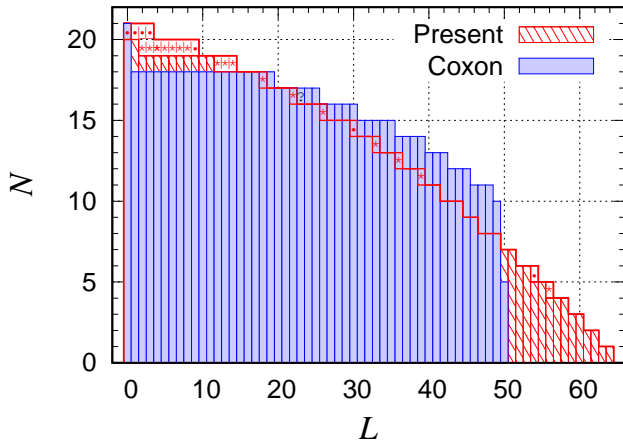
# HCl (18 electrons) - the first calculation



- (i) two-point Pade approximant  $\frac{1}{R} \text{Pade}[4/9](R)_{3,2}$  (red solid line)
- (ii) experimental data (red bullets)

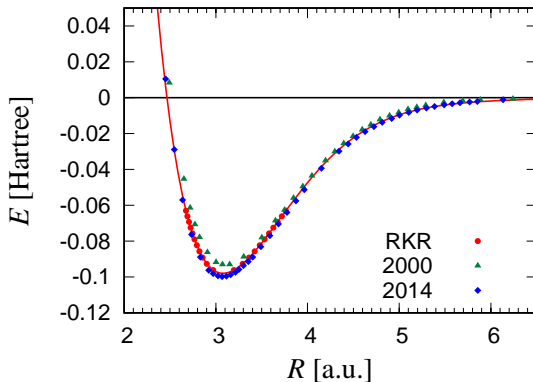
## HCl (18 electrons)

B-O rovibrational spectra for ground state – 836 states

 $\nu_{\max} = 20$  and  $L_{\max} = 64$

## CIF (26 electrons)

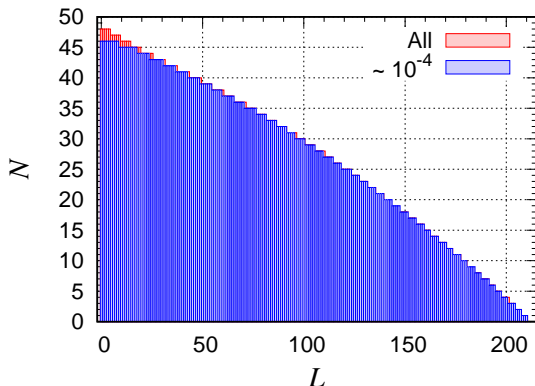
B-O potential energy for the ground state  $X^1\Sigma^+$



(i) the Padé approximant  $\frac{1}{R} \text{Pade}[4/9](R)_{3,2}$  (red line) (ii) RKR experimental data (red dots) (iii) points extracted from plots of numerical calculations: of 2000 (green triangles) and of 2014 (blue diamonds).

## CIF (26 electrons, the first calculation)

B-O rovibrational spectra for ground state – 5719 states (PREDICTION)



$$\nu_{max} = 210 \text{ and } L_{max} = 47$$

# Conclusions

- Exact B-O potential curve (the ground state eigenvalue of electronic Hamiltonian):

$$E_d(R) = \frac{1}{R} \frac{P_N^{(1)}}{Q_{N+3(5)}^{(1)}} - (R + \hat{\delta})^{\tilde{\delta}} e^{-\alpha R} \frac{P_{M_e}}{Q_{N_e}}$$

which looks like as a generalization of the Coulomb potential.

$E_d(R)$  exists inside of the accuracy of B-O approximation **ONLY!**

Theory of such potentials: periodic trajectories, symmetries, spectrum, exact solutions? - Open direction!

As the inventors of this potential we call it *TO potential*.