

Rational potentials and molecular physics

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

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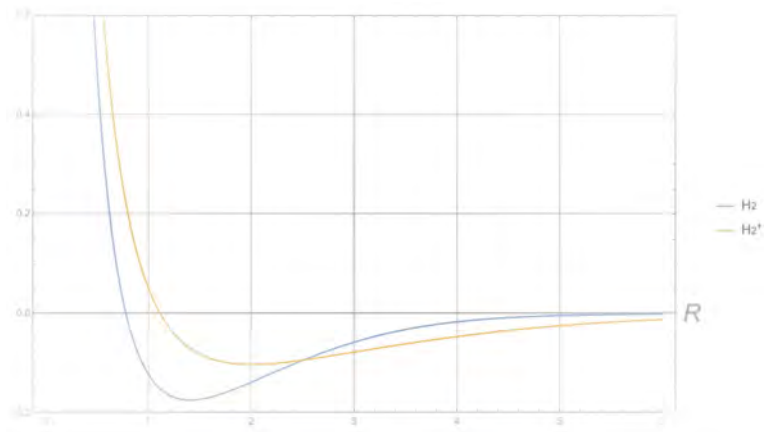
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- 2 (II) Positively charged homonuclear molecular ions $(A+A)^+$
- 3 Examples: H_2^+ and He_2^+
- 4 Rotational and vibrational states
- 5 Conclusions



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

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

μ is reduced mass

GOAL:

To construct analytical expression for the lowest potential energy curve

matching asymptotics at small and large R

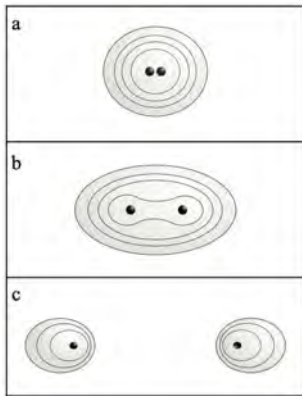
Physics Idea:

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)⁺

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 β 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_∞ 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!

ΔE (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 $\text{He}_2^+(\alpha, \alpha, 3e)$

(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

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

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

- $R \rightarrow 0$

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

- $R \rightarrow \infty$

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

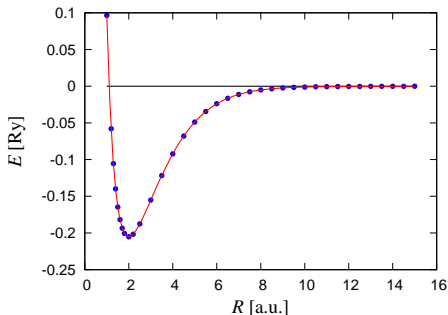
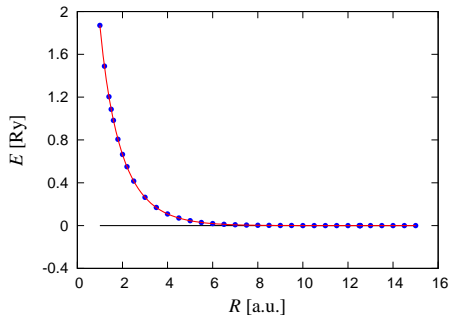
(one-instanton expansion, tunneling between Coulomb wells: J Cizek et al (1986))

- Interpolation: Padé approximant for ΔE

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

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

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

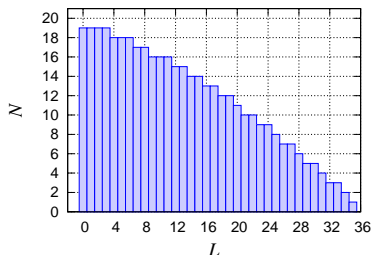
⇒ Lagrange Mesh Method

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 (ν, L)

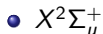
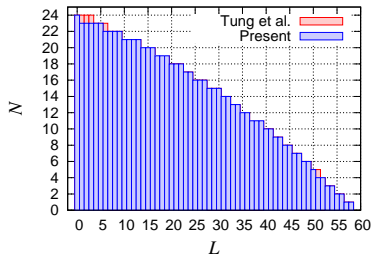
- $2p\sigma_u$

1 vibrational state ($1, 0$)

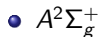
3 rotational states

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

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 (ν, L)

3-5 significant digits



3 vibrational states

6 rotational states

$$(\nu, L): \quad \nu = 0, 1, 2$$

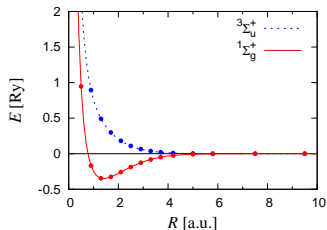
$$L = 0, \dots, 5$$

H₂

The ground and first excited state

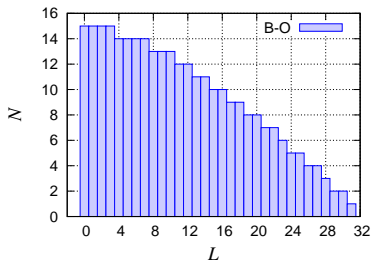
$$E(R) = \frac{1}{R} \text{Pade}_1[N/N + 5](R) \pm \frac{1}{2} e^{-2R} \text{Pade}_2[N + 5/N](R^{1/2})$$

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





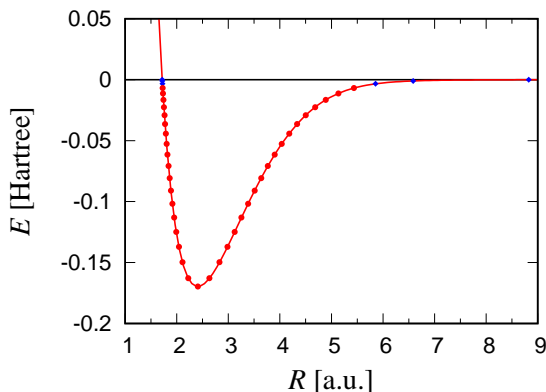
Ground state: 301 rovibrational states



3-5 significant digits

in agreement with exp.data!

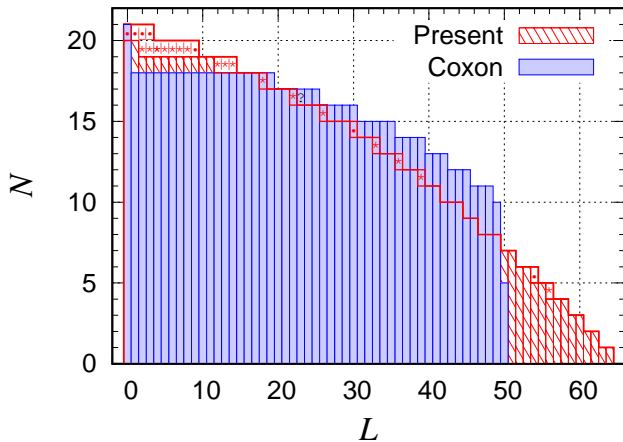
HCl (18 electrons) - the first calculation



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

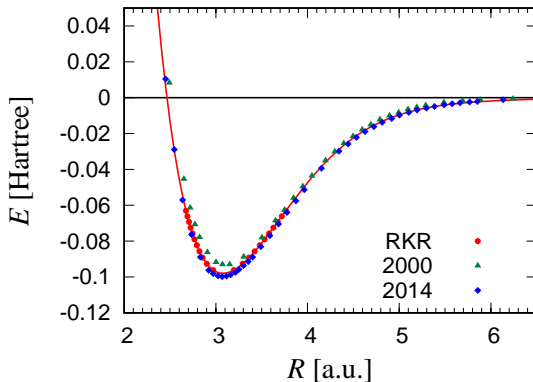
HCl (18 electrons)

B-O rovibrational spectra for ground state – 836 states

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

CIF (26 electrons)

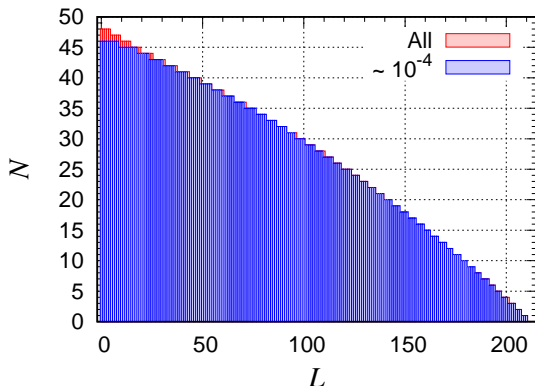
B-O potential energy for the ground state $X^1\Sigma^+$



(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*.