Nuclear Potential Energy Functions

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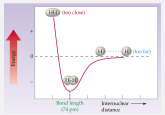
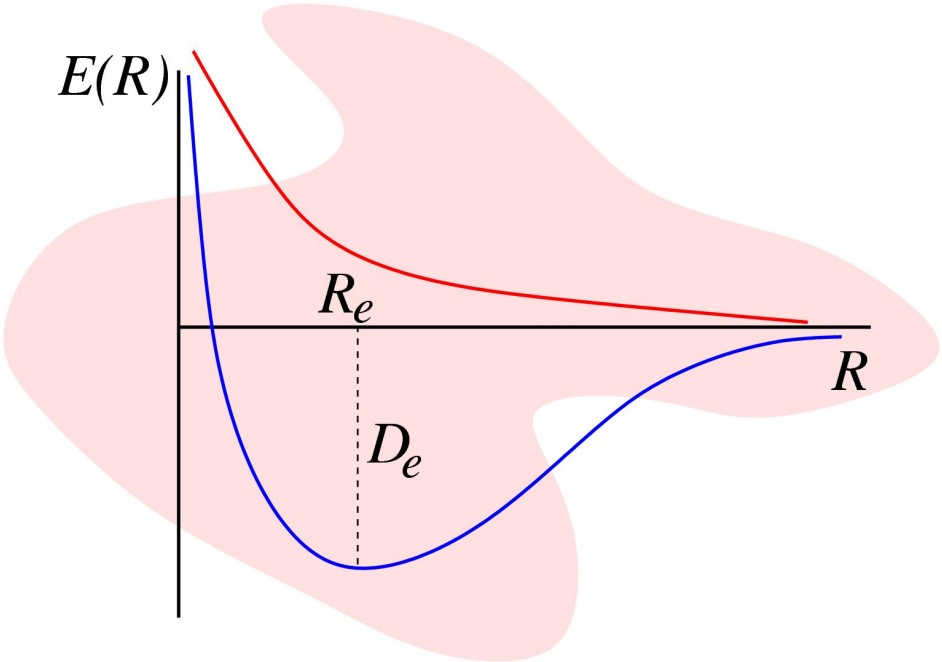
Born-Oppenheimer approximation

- Molecular Hamiltonian $\Rightarrow \hat{H}(\mathbf{r},\mathbf{R}) = \hat{T}_{\mathrm{e}}(\mathbf{r}) + \hat{T}_{\mathrm{N}}(\mathbf{R}) + \hat{V}(\mathbf{r},\mathbf{R})$
- BO approximation:
  - $\psi(\mathbf{r},\mathbf{R},t) = \underbrace{\phi_j^{\mathrm{BO}}(\mathbf{r},\mathbf{R})}_{\text{electronic}}\,\underbrace{\Omega(\mathbf{R},t)}_{\text{nuclear}}$
  - $\left[\hat{T}_{\mathrm{e}}(\mathbf{r}) + \hat{V}(\mathbf{r},\mathbf{R})\right]\phi_j^{\mathrm{BO}}(\mathbf{r},\mathbf{R}) = \epsilon_j^{\mathrm{BO}}(\mathbf{R})\,\phi_j^{\mathrm{BO}}(\mathbf{r},\mathbf{R})$
  - $i\hbar\frac{\partial\Omega(\mathbf{R},t)}{\partial t} = \left[\hat{T}_{\mathrm{N}}(\mathbf{R}) + \epsilon_j^{\mathrm{BO}}(\mathbf{R})\right]\Omega(\mathbf{R},t)$
- Grid $\{R_i\}_{i=1}^N \Rightarrow \{\epsilon_j^{\mathrm{BO}}(R_i)\}_{i=1}^N$



Potential energy curve

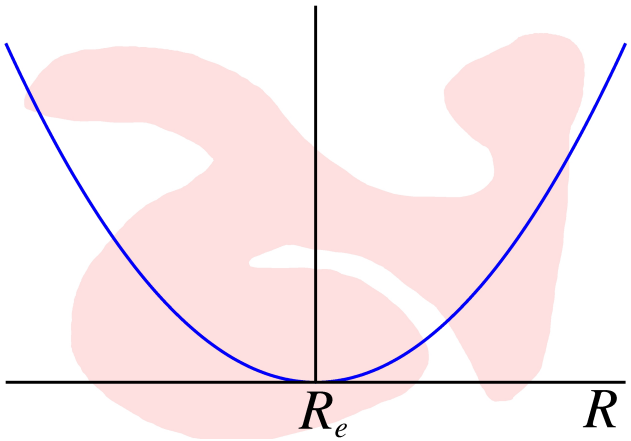


- Unbound states.
- Bound states.
  - Dissociation energy $\Rightarrow D_e$
  - Internuclear equilibrium distance $\Rightarrow R_e$ (bond length)

- Potential energy curve

$$V(R) = \underbrace{V(R_e)}_{\text{energy origin}} + \underbrace{\left(\frac{\partial V}{\partial R}\right)_{R_e}}_{\text{minimun}}(R-R_e) + \frac{1}{2}\left(\frac{\partial^2 V}{\partial R^2}\right)_{R_e}(R-R_e)^2 + \frac{1}{6}\left(\frac{\partial^3 V}{\partial R^3}\right)_{R_e}(R-R_e)^3 + \text{higher order terms}$$

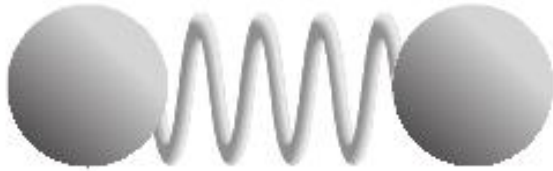
Harmonic oscillator



- Harmonic potential

$$V_{\mathrm{h}}(R) = \frac{1}{2} \underbrace{\left(\frac{\partial^2 V}{\partial R^2}\right)_{R_e}}_{k \to \text{force constant}} \underbrace{(R - R_e)^2}_{q}$$

- $\lim_{R\to\infty} V_{\mathrm{h}}(R) = \infty \neq D_e$
- Minimun at $R = R_e$
- $\lim_{R\to 0} V_{\mathrm{h}}(R) = \frac{1}{2} k R_e^2 < \infty$



Hooke's law

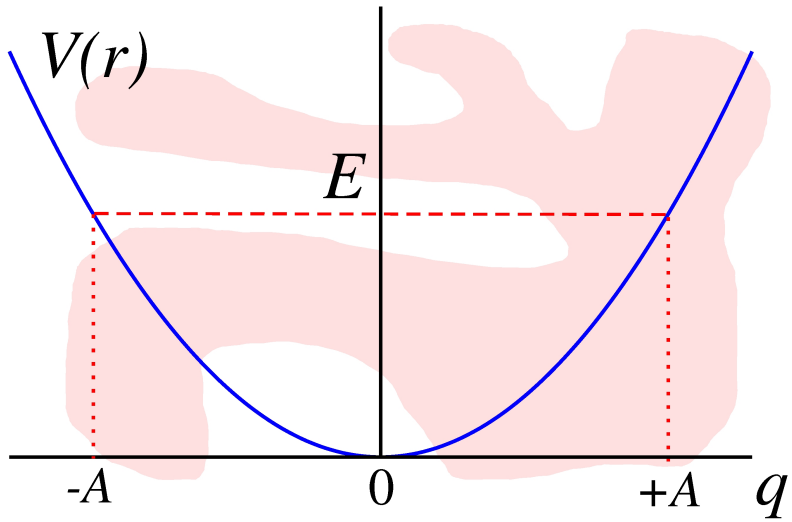
$$F = -\frac{dV_{\mathrm{h}}}{dq} = -k\, q_{\mathrm{h}}$$

Harmonic oscillator (HO)

- Classical HO

$$E = \frac{p_{\mathrm{h}}^2}{2\mu} + \frac{1}{2}kq_{\mathrm{h}}^2 = \frac{1}{2}kA^2$$

$$\mu = \frac{m_A m_b}{m_A + m_B}$$

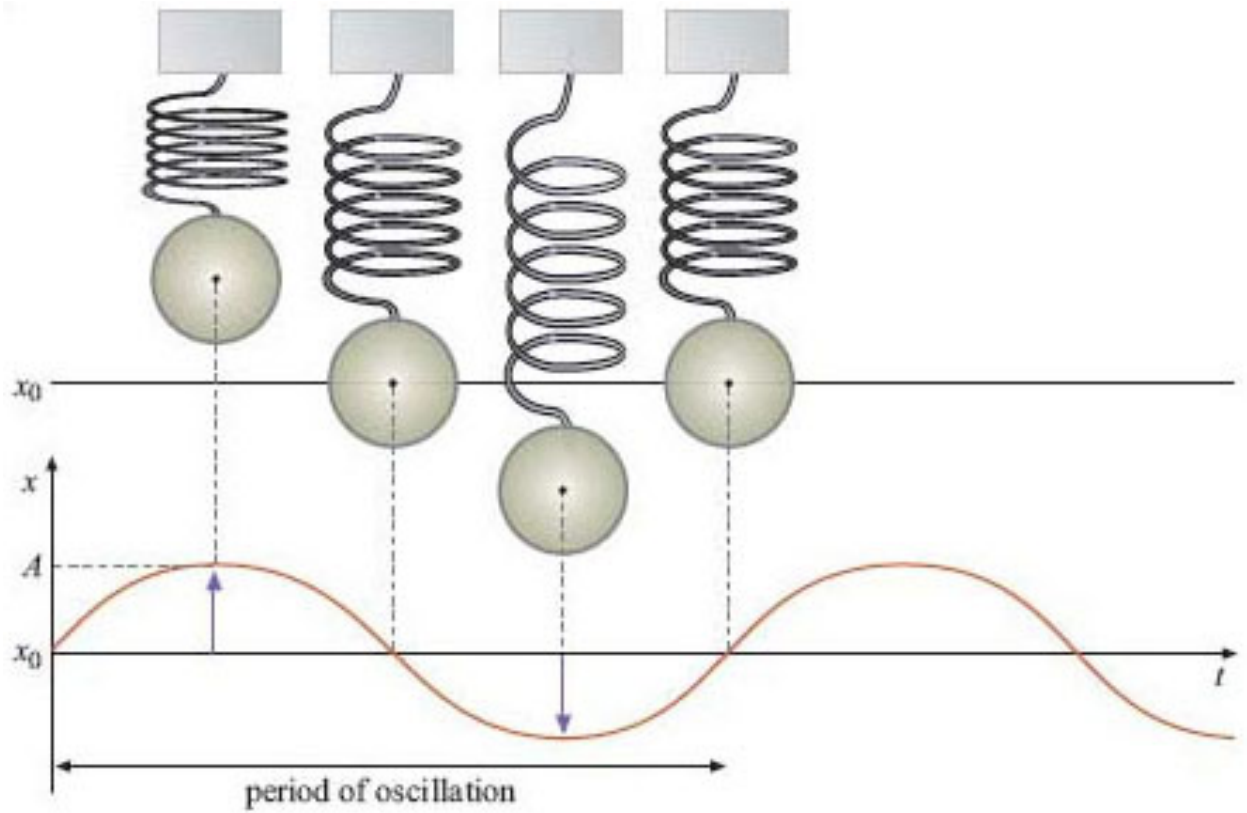


$$F = -k\,q_{\mathrm{h}} = \mu\,a \rightarrow -k\,q_{\mathrm{h}} = \mu\frac{d^2 q_{\mathrm{h}}}{dt^2}$$

$$\downarrow \quad q_{\mathrm{h}}(0)=0$$

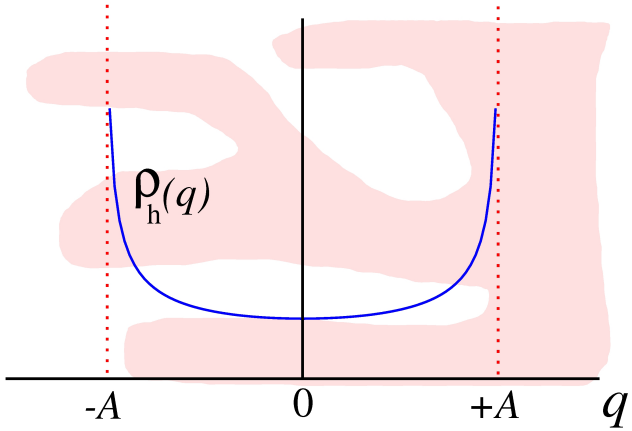
$$q_{\mathrm{h}}(t) = A\,\sin(\omega t) \rightarrow \omega = 2\pi\nu = \sqrt{k/\mu}$$

Harmonic oscillator (HO)



Harmonic oscillator (HO)

$$p_{\mathrm{h}}(t) = \mu\,\dot{q}_{\mathrm{h}}(t) = \mu A\omega\cos(\omega t) = \mu\omega\sqrt{A^2 - q_{\mathrm{h}}^2(t)}$$



$$\rho_{\mathrm{h}}(q) \propto \frac{1}{p_{\mathrm{h}}(t)}$$

$$\downarrow$$

$$\rho_{\mathrm{h}}(q) = \frac{1}{\pi\sqrt{A^2 - q_{\mathrm{h}}^2(t)}}$$

$$\rho_{\mathrm{h}}(p) = \frac{1}{\pi\sqrt{p_{\mathrm{max}}^2 - p_{\mathrm{h}}^2(t)}}$$

R.W. Roninette, Am. J. Phys. **63**, 823 (1995)

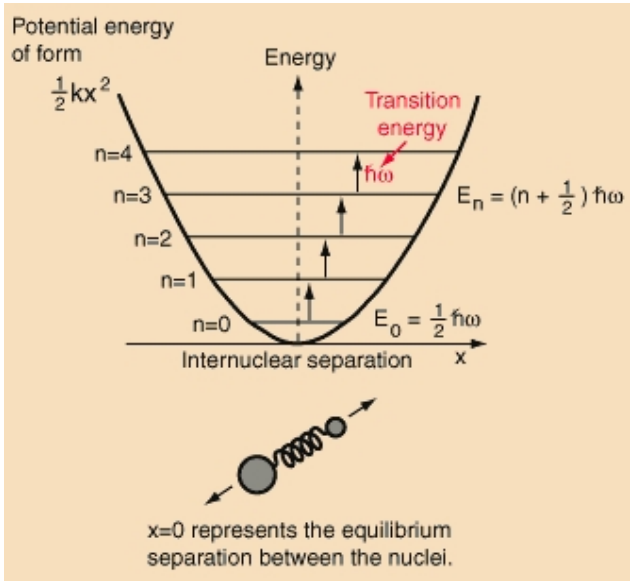
Harmonic oscillator (HO)

- Quantum HO

$$\hat{H}_{\mathrm{h}}(q) = -\frac{\hbar^2}{2\mu}\frac{d^2}{dq^2} + \frac{1}{2}kq^2 \rightarrow \quad \hat{H}_{\mathrm{h}}(q)\phi_n^{\mathrm{h}}(q) = E_n^{\mathrm{h}}\phi_n^{\mathrm{h}}(q)$$

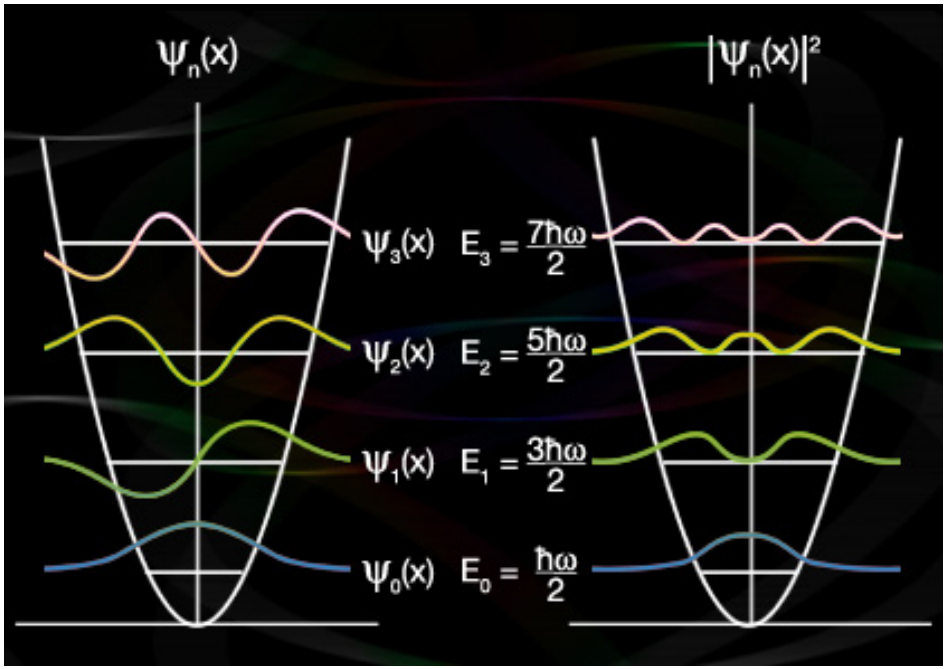
$\Rightarrow$ HO eigenvalues

- $E_n^{\mathrm{h}} = (n + \frac{1}{2})\, h\nu \qquad n = 0, 1, 2, \ldots$
- Minimun energy $\rightarrow E_0^{\mathrm{h}} = \frac{1}{2}\, h\nu \rightarrow$ Zero-point energy (ZPE)
- $\Delta E = E_{n+1} - E_n = h\nu \rightarrow$ vibrational quantum



Harmonic oscillator (HO)

$\Rightarrow$ HO wavefunctions



$$\phi_0(q) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha q^2/2}$$

$$\phi_1(q) = \left(\frac{4\alpha^3}{\pi}\right)^{1/4} q\, e^{-\alpha q^2/2}$$

$$\phi_2(q) = \left(\frac{\alpha}{4\pi}\right)^{1/4} (1 - 2\alpha q^2)\, e^{-\alpha q^2/2}$$

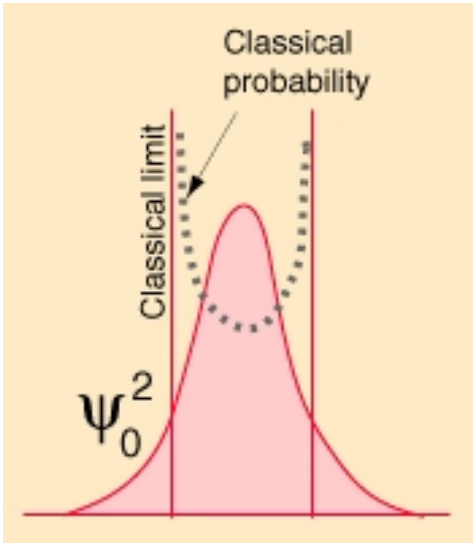
$$\alpha = \frac{2\pi\nu\mu}{\hbar}$$

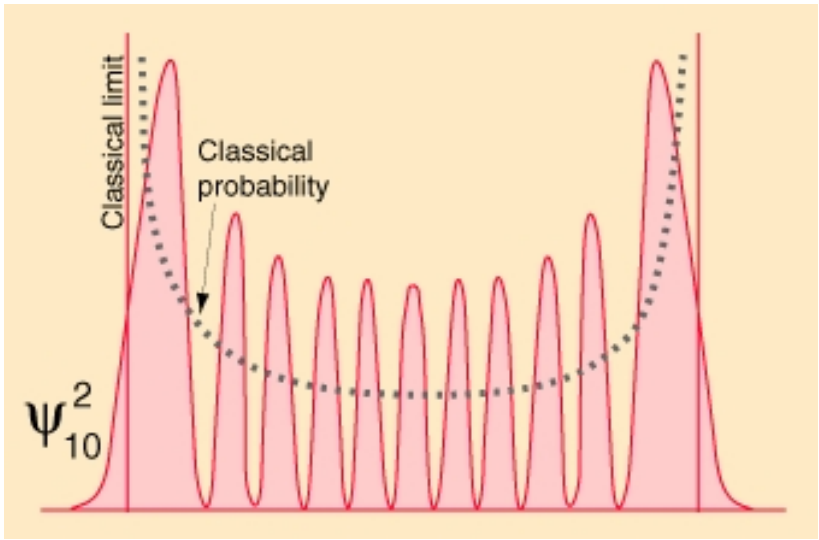
- Nodes $\Rightarrow n$

Harmonic oscillator (HO)

- Classicaly allowed and forbidden regions

$$E = T + V \xrightarrow{T \geqslant 0} E \geqslant V \rightarrow -A \leq q_{\mathrm{cl}}^{\mathrm{h}} \leq +A$$





Harmonic oscillator (HO)

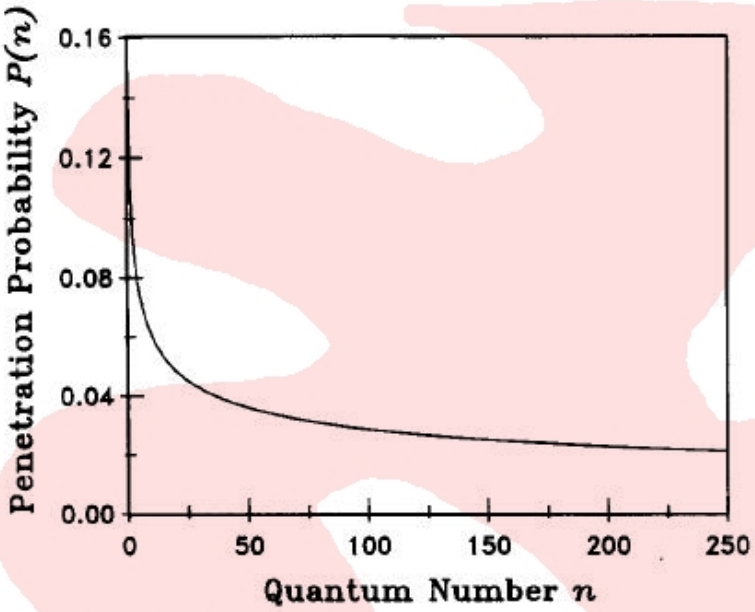
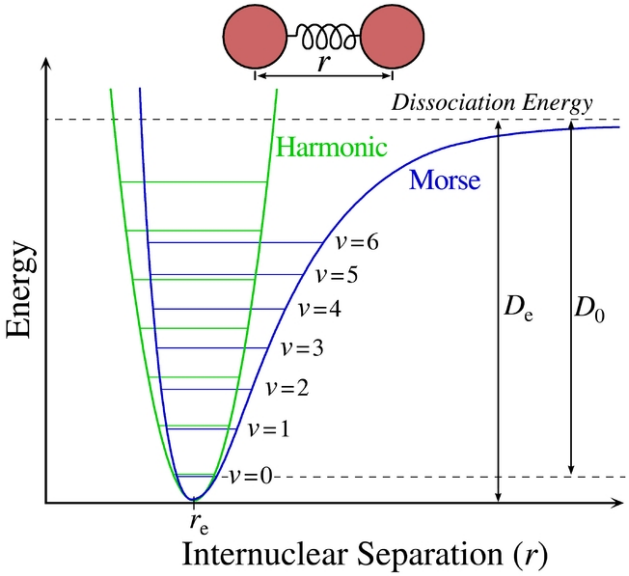


Fig. 1. The graph of the penetration probability $P(n)$ vs quantum number n for values of n ranging from $n=0$ to $n=250$.

▷ J.J. Diamond, Am. J. Phys. **60**, 912 (1992)

- Problems
  - No dissociation limit ($\uparrow n$)
  - Anharmonicities $\Rightarrow k_3\, q^3 + k_4\, q^4 + \ldots \rightarrow \Delta E \neq$ constant

Morse oscillator



- $\lim_{r\to\infty} V_{\mathrm{M}}(r)=D_e$
- Minimun at $r = r_e$
- $\lim_{r\to 0} V_{\mathrm{M}}(r)=D_e\left(1-e^{aR_e}\right)^2<\infty$

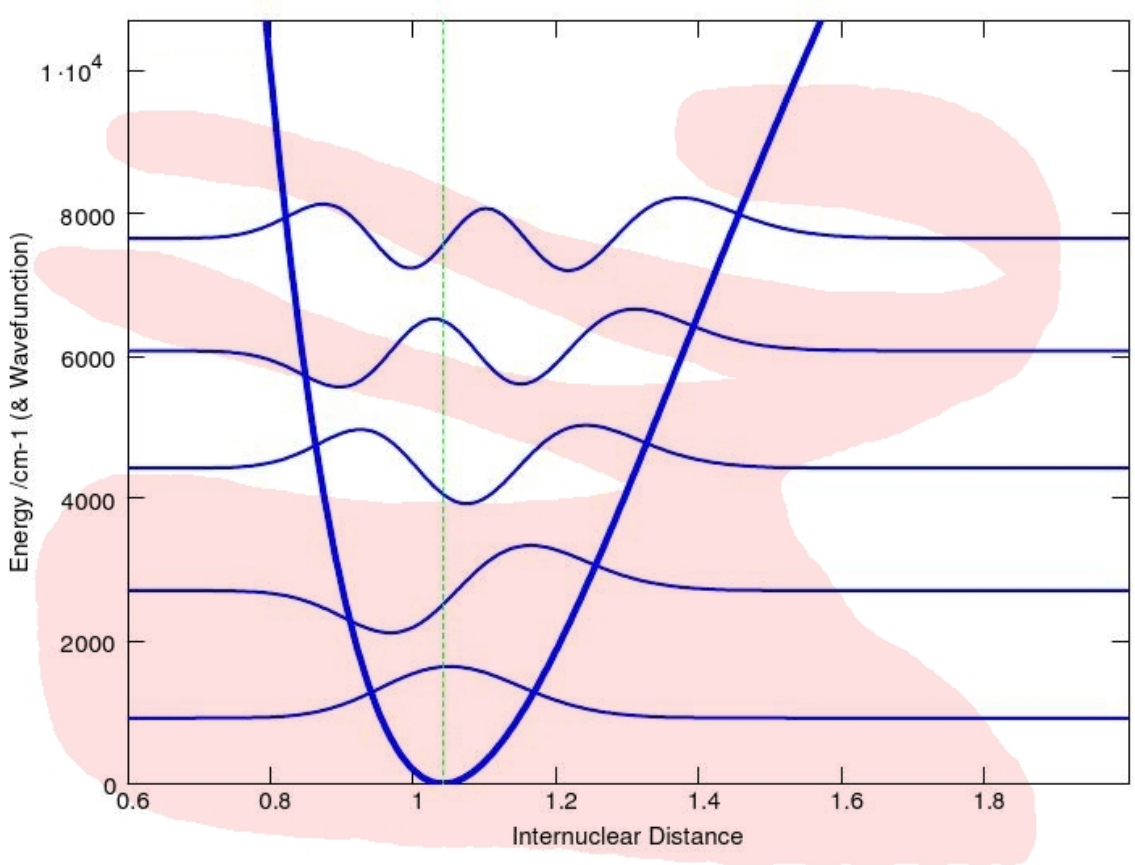
- Philip McCord Morse, (August 6, 1903 - September 5, 1985)

$$V_{\mathrm{M}}(R) = D_e\left(1 - e^{-a(R-R_e)}\right)^2$$

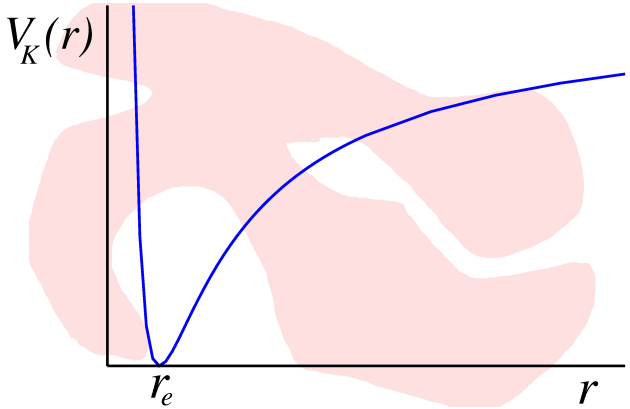
- $E_n=4D_e\left[\frac{n+1/2}{S}-\left(\frac{n+1/2}{S}\right)^2\right]$
- ZPE $\Rightarrow D_0 = D_e - E_0$
- $\Delta E = \frac{4D_e}{S}\left(1 - \frac{2(n+1)}{S}\right)$
- $S = \sqrt{8\mu D_e}/a\hbar$

Morse oscillator

- Morse wavefunctions



Kratzer oscillator



- $\lim_{r\to\infty} V_{\mathrm{K}}(r) = D_e$
- Minimun at $r = r_e$
- $\lim_{r\to 0} V_{\mathrm{M}}(r) = \infty$

- B. Adolf Kratzer (1893-1983)

$$V_{\mathrm{K}}(R) = D_e\left(1 - \frac{r_e}{r}\right)^2$$

- $E_n = D_e\left(1 - \frac{D_e/B_e}{(n+m+1)^2}\right)$

$$m = \left(\frac{D_e}{B_e} + \frac{1}{4}\right)^{1/2} - \frac{1}{2} \quad \text{and} \quad B_e = \frac{\hbar^2}{2\mu r_e^2}$$

- $\Delta E = \frac{D_e^2}{B_e}\left(\frac{1}{(n+m+1)^2} - \frac{1}{(n+m+2)^2}\right)$

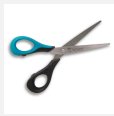
Other oscillators

- Analytic: Rosen-Morse, Rydberg, Linnett, ...
- Power series expansions:

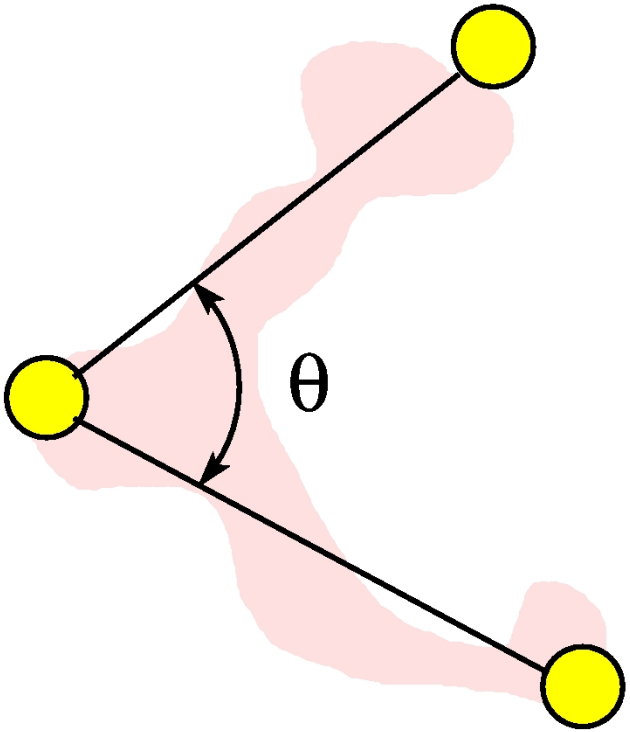
$$V(y) = V(0) + \left(\frac{\partial V}{\partial y}\right)_0 y + \frac{1}{2!}\left(\frac{\partial^2 V}{\partial y^2}\right)_0 y^2 + \frac{1}{3!}\left(\frac{\partial^3 V}{\partial y^3}\right)_0 y^3 + \dots$$

$$y = R - R_e, 1 - e^{-a(R-R_e)}, \frac{R - R_e}{R}, \dots$$

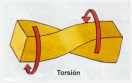
- Many adjustable parameters. Quality of the fit $\Leftrightarrow$ Uncertainty
- Numerical solution of the vibrational Schrödinger equation.



Bending vibrations

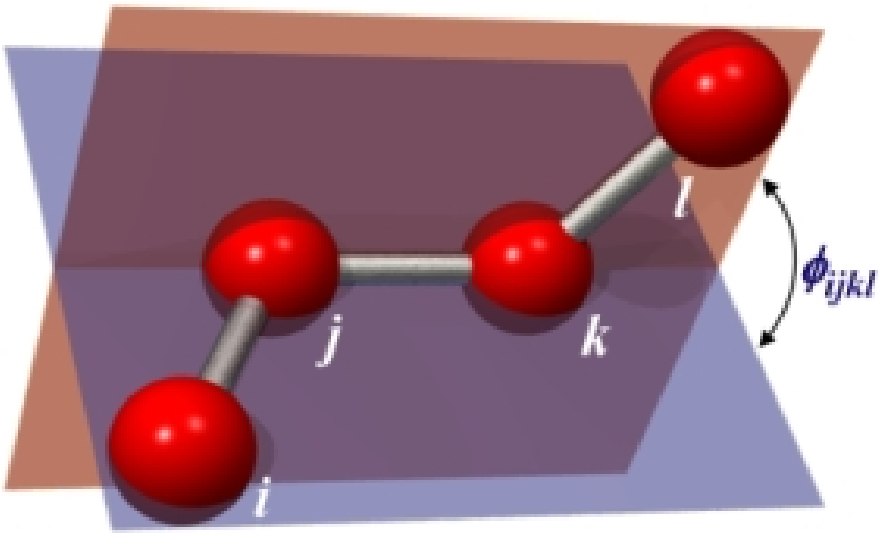


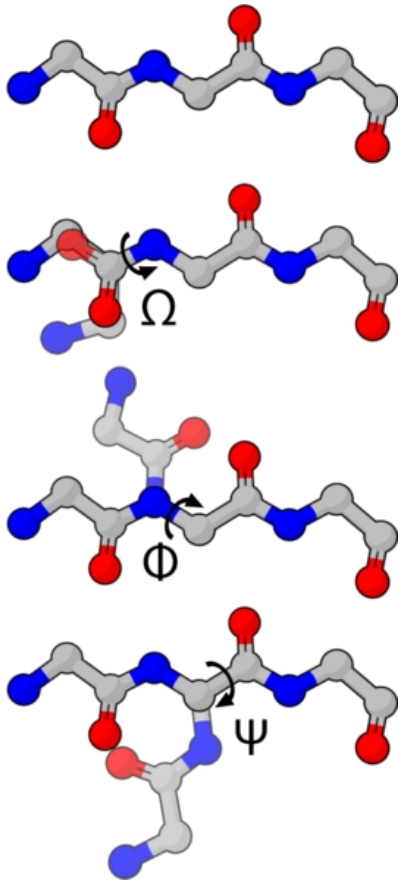
- Harmonic bending vibrations
  - $V(\theta) = \frac{1}{2} k (\theta - \theta_e)^2$
  - $F_\theta = -k (\theta - \theta_e)$
- Anharmonic terms
  $\Rightarrow k_3 (\theta - \theta_e)^3 + \ldots$

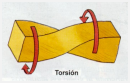


Torsional motions

- Dihedral angles

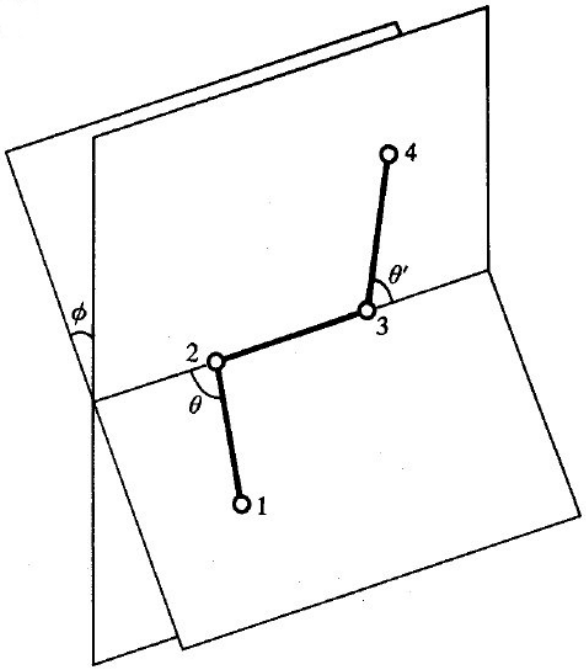


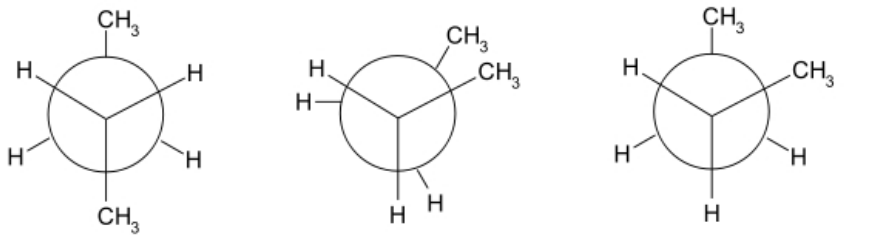


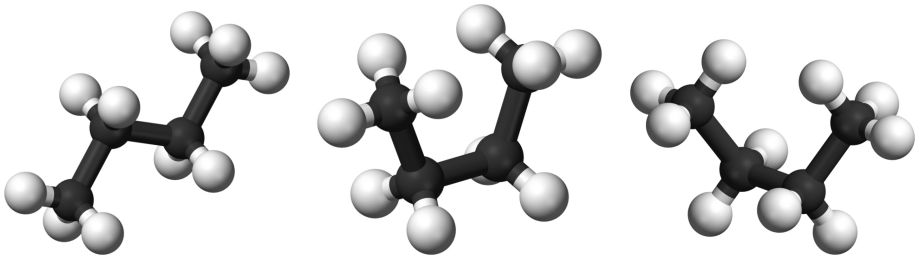


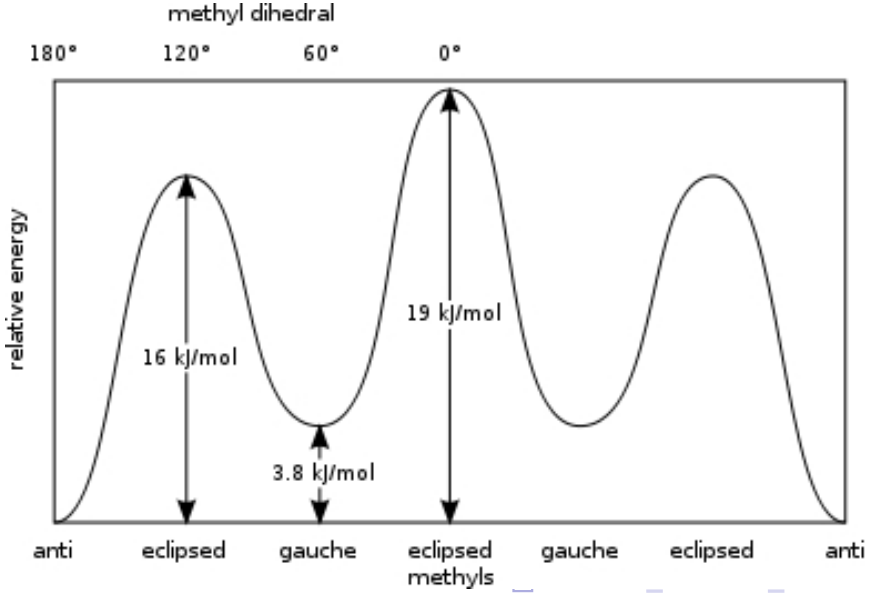
Torsional motions

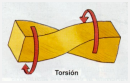
- Torsional motions





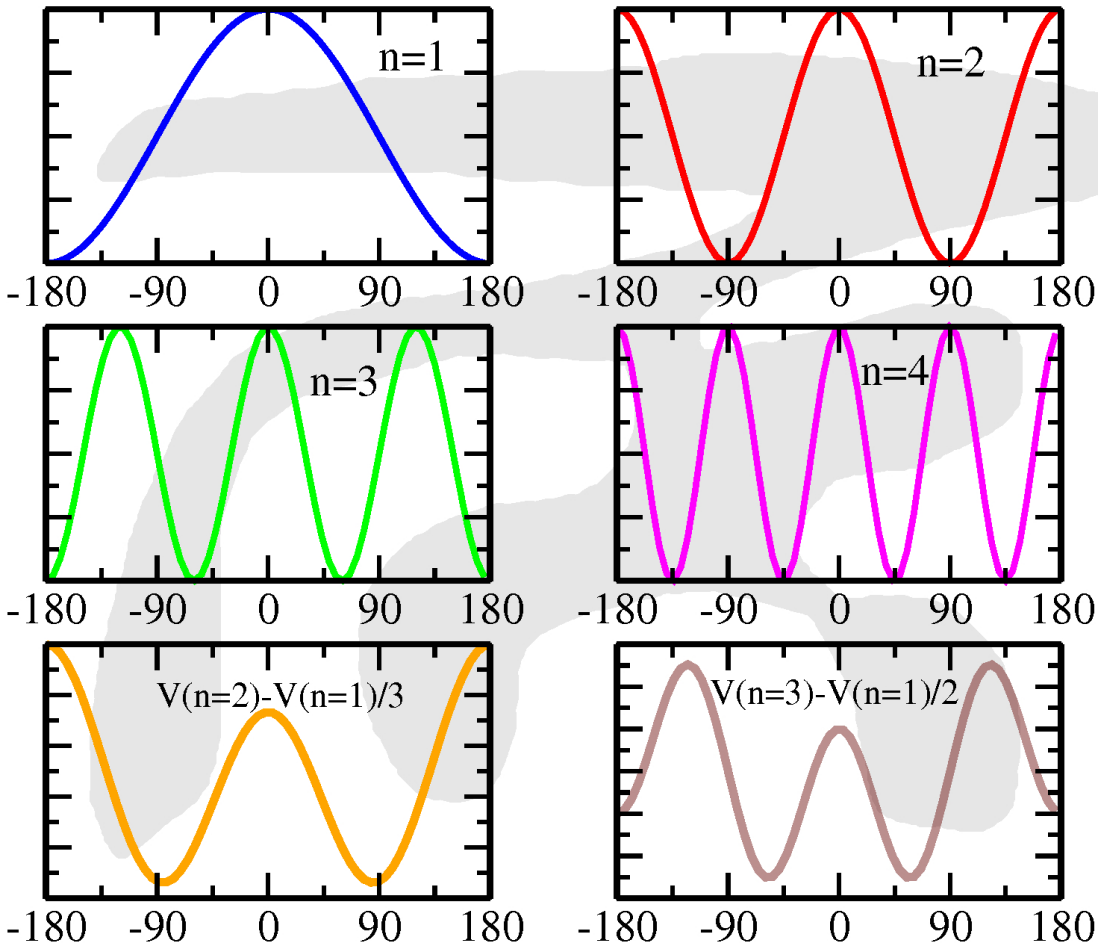




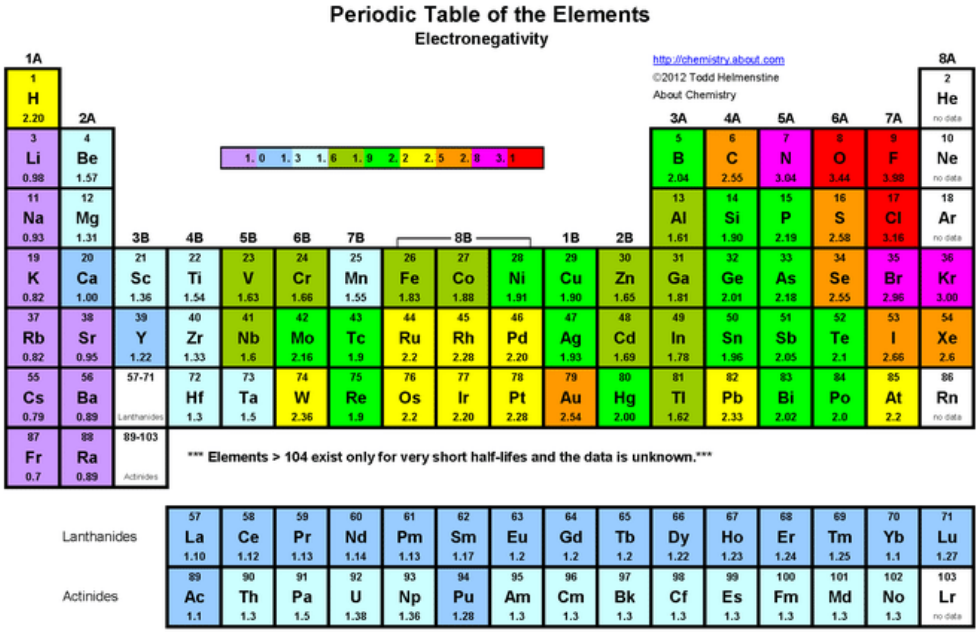


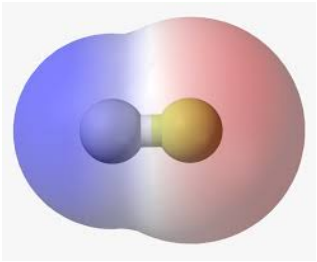
Torsional motions

$$V(\phi) = \frac{1}{2}\, k\, (1 + \cos(n\,\phi + \gamma))$$



Coulomb forces

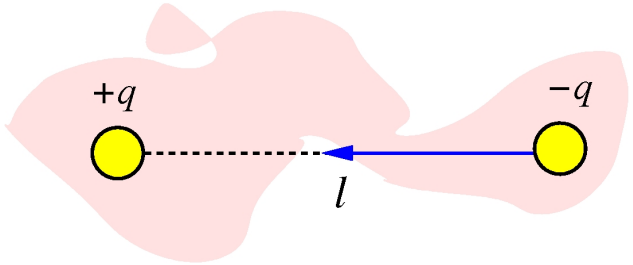




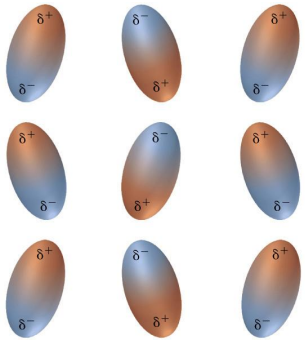
- $V(r_{ij}) = \frac{1}{4\pi\epsilon_0}\frac{q_i\, q_j}{r_{ij}}$
- $-e < q_i, q_j < +e$

van der Waals forces

- van der Waals forces
  - Electric dipole $\Rightarrow \mu = q \cdot l$

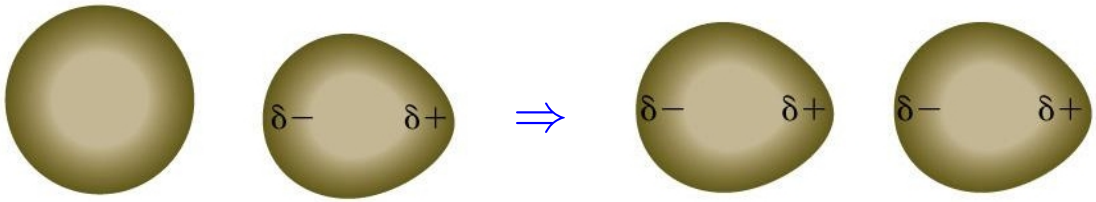


  - Dipole-dipole interactions



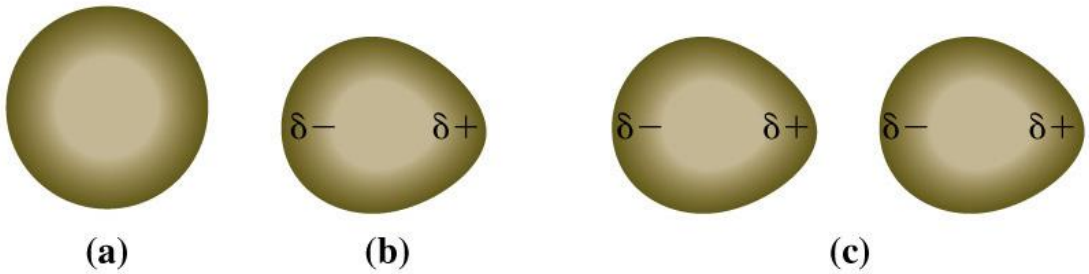
$$V_{\mathrm{dd}} = -\frac{C}{r^6} \rightarrow C \propto \frac{\mu_1 \mu_2}{T}$$

  - Dipole-induced dipole interactions



van der Waals forces

- Instantaneous dipole-induced dipole interactions.
  Ej. $He_{(l)}$, $Ne_{(l)}$, ...

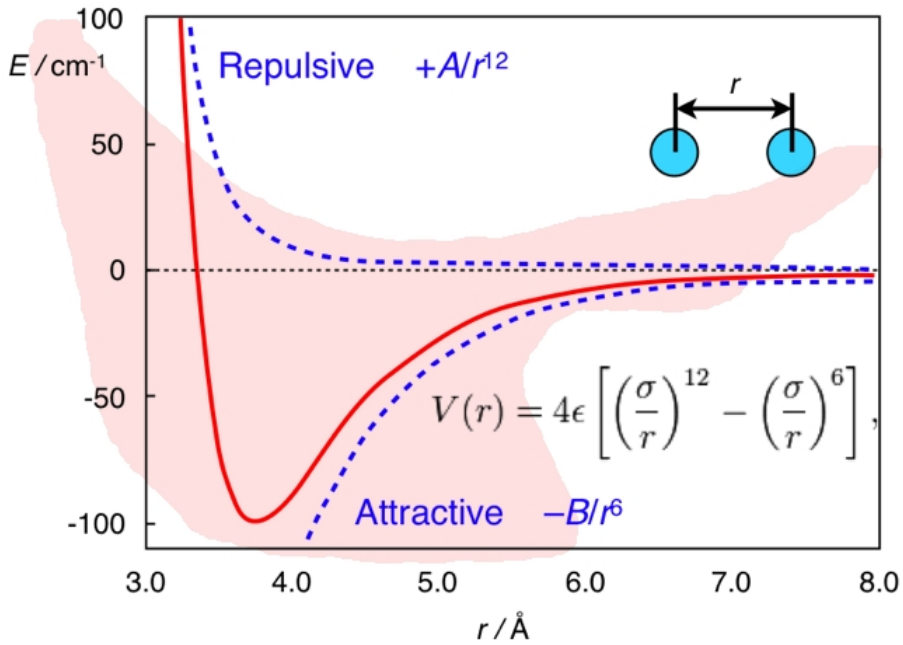


$V_{dd} = -\frac{C}{r^6} \rightarrow C \propto \frac{\alpha_1 \alpha_2}{T} \rightarrow \alpha$ polarizability

- Intensity $\Rightarrow$ dipole-dipole $>$ dipole-ind. dipole $>$ inst. dipole-ind. dipole
- Short range repulsive forces $\Rightarrow V_{rep} \propto \frac{1}{r^{12}}$

van der Waals forces

- Lennard-Jones potential



- $V_{\mathrm{LJ}}(r) = 4\epsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right) = \epsilon\left(\left(\frac{r_{\min}}{r}\right)^{12} - 2\left(\frac{r_{\min}}{r}\right)^{6}\right)$
- $r_{\min} = 2^{1/6}\,\sigma \Rightarrow V_{\mathrm{LJ}}(r_{\min}) = -\epsilon$
- $V_{\mathrm{LJ}}(\sigma) = 0 \Rightarrow$ effective atomic radius

van der Waals forces

- Homoatomic interactions

Table 1.1. *Atom–atom interaction parameters*

Atom	Source	ε/k_B(K)	σ(nm)
H	[Murad and Gubbins 1978]	8.6	0.281
He	[Maitland *et al.* 1981]	10.2	0.228
C	[Tildesley and Madden 1981]	51.2	0.335
N	[Cheung and Powles 1975]	37.3	0.331
O	[English and Venables 1974]	61.6	0.295
F	[Singer *et al.* 1977]	52.8	0.283
Ne	[Maitland *et al.* 1981]	47.0	0.272
S	[Tildesley and Madden, 1981]	183.0	0.352
Cl	[Singer *et al.* 1977]	173.5	0.335
Ar	[Maitland *et al.* 1981]	119.8	0.341
Br	[Singer *et al.* 1977]	257.2	0.354
Kr	[Maitland *et al.* 1981]	164.0	0.383

- Heteroatomic interactions

$$\sigma_{AB} = \frac{1}{2}\left(\sigma_A + \sigma_b\right) \qquad \epsilon_{AB} = \sqrt{\epsilon_A \cdot \epsilon_B}$$

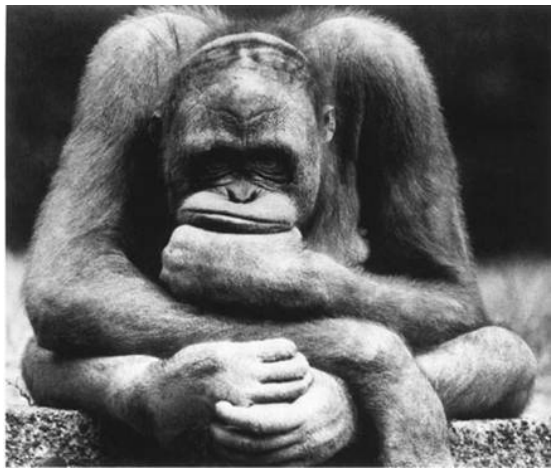
Criteria

- Any fragment of the molecule

$$ABC \rightarrow A + BC$$
$$\rightarrow B + AC$$
$$\rightarrow C + AB$$
$$\rightarrow A + B + C$$

- Symmetry properties
- Reproduce experimental/*ab initio* data
- Reasonable behaviour everywhere
- Smooth behaviour

- Simple algebraic form
- Easy to fit
- Good convergence with new data
- Focus on most meaningful regions
- ⋮



Power series expansions

$$V = V_{\mathrm{eq}} + \sum_i \left(\frac{\partial V}{\partial q_i}\right)_{\mathrm{eq}} q_i + \frac{1}{2!}\sum_{i,j}\left(\frac{\partial^2 V}{\partial q_i \partial q_j}\right)_{\mathrm{eq}} q_i q_j + \frac{1}{3!}\sum_{i,j,k}\left(\frac{\partial^3 V}{\partial q_i \partial q_j \partial q_k}\right)_{\mathrm{eq}} q_i q_j q_k + \ldots$$

- Convergence properties $\Rightarrow$ dissociation channels
- Many parameters $\rightarrow$ accurate
- Difficult interpretation
- Spectroscopy

Power series expansions

Journal of Molecular Structure (Theochem), 166 (1988) 357–362
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

PERTURBED MORSE EXPANSION FOR TRIATOMIC MOLECULES

J. Zúñiga, A. Bastida, A. Hidalgo and A. Requena
Departamento de Química-Física, Universidad de Murcia, Murcia 30001 (España)

lengths. The most commonly used expansion has been that in terms of internal displacements coordinates

$$V_R = \sum K_{ij}R_iR_j + \sum K_{ijk}R_iR_jR_k + \sum K_{ijkl}R_iR_jR_kR_l \qquad (1)$$

where $R_1=r_1-r_{1,e}$, $R_2=\theta-\theta_e$ and $R_3=r_3-r_{3,e}$ which is adequate around

POTENTIAL MODEL

The internuclear motion of a triatomic molecule can be described

$$V_M = \sum M_{ij}y_iy_j + \sum M_{ijk}y_iy_jy_k + \sum M_{ijkl}y_iy_jy_ky_l \qquad (2)$$

where

$$y = 1 - e^{-a_i(r_i-r_{i,e})} \qquad i = 1,3 \qquad (3)$$

and

$$y_2 = \theta - \theta_{eq.} \qquad (4)$$

Many-body expansions

$$V = \sum_{i<j} V_2(r_{ij}) + \sum_{i<j<k} V_3(r_{ij}, r_{ik}, r_{jk}) + \ldots$$

$r_{ij} \rightarrow$ distance between atoms i and j

$V_2 \rightarrow$ Two body interactions

$V_3 \rightarrow$ Three body interactions

- Good asymptotic behaviour
- Low flexibility in bond regions
- Useful in reactivity

ELSEVIER

17 February 1995

Chemical Physics Letters 233 (1995) 405–410

CHEMICAL PHYSICS LETTERS

Adjusted double many-body expansion potential energy surface for HO_2 based on rigorous vibrational calculations

A.J.C. Varandas [a], J.M. Bowman [a,1], B. Gazdy [b]

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Received 10 November 1994; in final form 29 November 1994

Molecular Mechanics potentials

$$V = \sum_{\text{bonds}} \frac{1}{2} k_b (l - l_0)^2 + \sum_{\text{angles}} \frac{1}{2} k_a (\theta - \theta_0)^2 + \sum_{\text{torsions}} \frac{1}{2} V_n [1 + \cos(n\omega - \gamma)]$$

$$+ \sum_{j=1}^{N-1} \sum_{i=j+1}^{N} \left\{ \epsilon_{i,j} \left[\left(\frac{r_{0ij}}{r_{ij}} \right)^{12} - 2 \left(\frac{r_{0ij}}{r_{ij}} \right)^{6} \right] + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \right\}$$

- Biomolecules (proteins, ADN,...)
- Very general
- Accuracy

Molecular Mechanics potentials

- AMBER ⇒ Assisted Model Building with Energy Refinement
  W.D. Cornell *et al. A second generation force field for the simulation of proteins, nucleic acids and organic molecules*. J. Am. Chem. Soc. **117**, 5179-5197 (1995).
- CHARMM ⇒ CHemistry At HaRvard Molecular Mechanics
  small M. Karplus *et al. All-atom empirical potential for molecular modeling and dynamics studies of proteins*. J. Phys. Chem. **102**, 3586-3616 (1998).
- GROMOS ⇒ GROningen MOlecular Simulation
  van Gunsteren *et al. A biomolecular force field based on the free enthalpy of hydratation and solvation: The GROMOS force field parameter sets 53A5 and 53A6*. J. Comput. Chem. **25**, 1656-1676 (2004).
- OPLS ⇒ Optimized Potential for Liquid Simulations
  W.L. Jorgensen *et al. Development and testing of the OPLS all-atom force field on conformational energetics and properties of organic liquids*. J. Am. Chem. Soc. **118**, 11225-11236 (1996).

Molecular Mechanics potentials

The Nobel Prize in Chemistry 2013
Martin Karplus, Michael Levitt, Arieh Warshel

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The Nobel Prize in Chemistry 2013

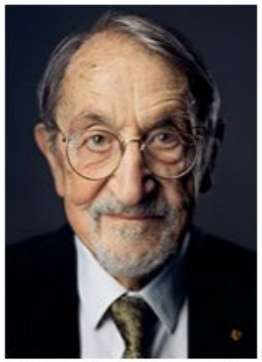


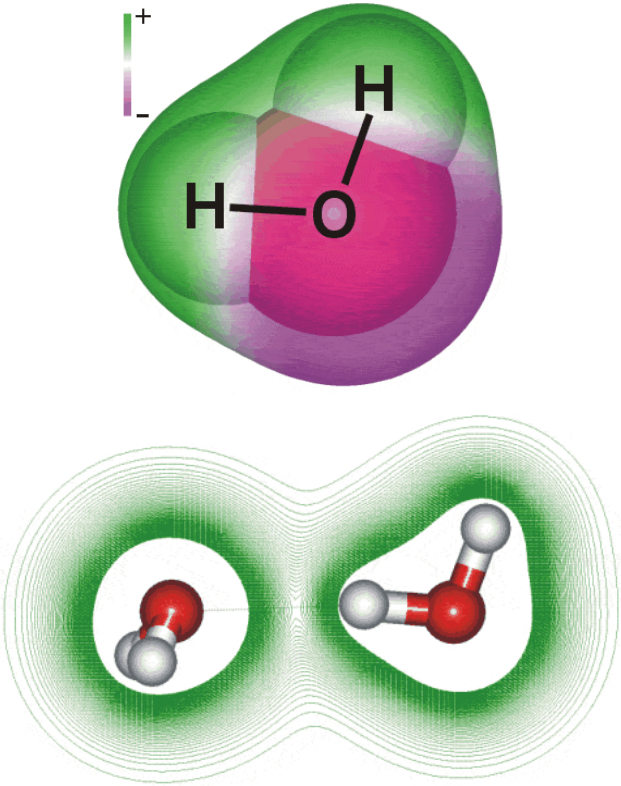
Photo: A. Mahmoud
Martin Karplus
Prize share: 1/3


Photo: A. Mahmoud
Michael Levitt
Prize share: 1/3


Photo: A. Mahmoud
Arieh Warshel
Prize share: 1/3

The Nobel Prize in Chemistry 2013 was awarded jointly to Martin Karplus, Michael Levitt and Arieh Warshel *"for the development of multiscale models for complex chemical systems"*.

Water

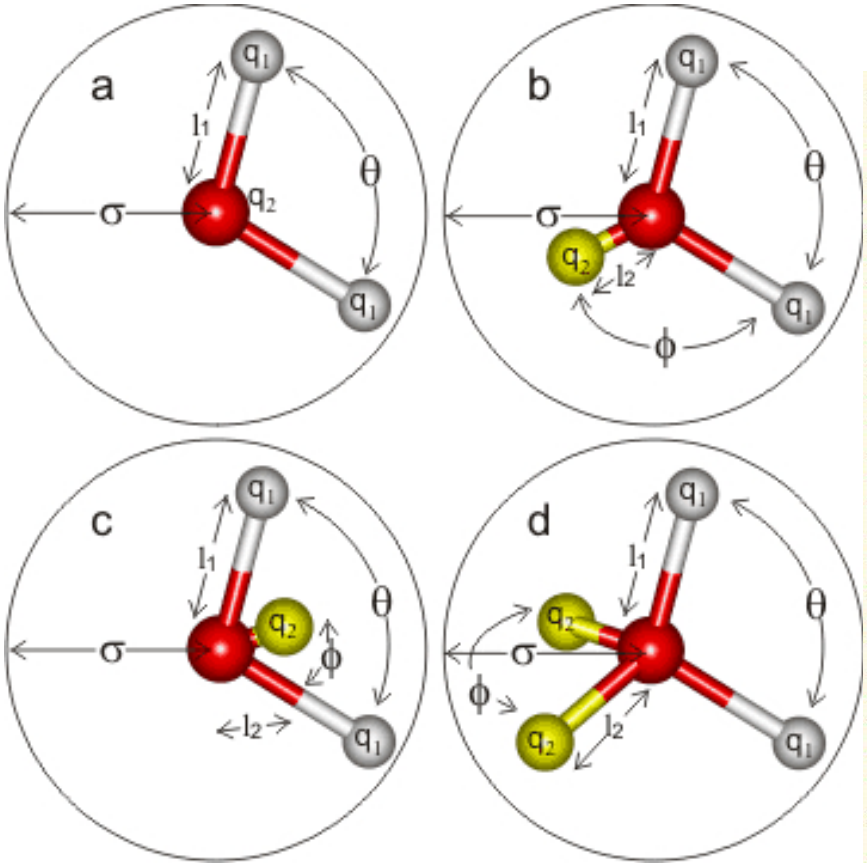


- Most studied molecule
  $\Rightarrow$ H-bond
- 69 anomalous properties of water

http://www1.lsbu.ac.uk/water/water_anomalies.html

Water

- Models



Parameters for some water molecular models

Model	Type	σ Å [6]	ε kJ mol^{-1} [6]	l_1 Å	l_2 Å	q_1 (e)	q_2 (e)	θ°	φ°
SSD [511]	-[8]	3.016	15.319	-	-	-	-	109.47	109.47
SPC [94]	a	3.166	0.650	1.0000	-	+0.410	-0.8200	109.47	-
SPC/E [3]	a	3.166	0.650	1.0000	-	+0.4238	-0.8476	109.47	-
SPC/HW (D_2O) [220]	a	3.166	0.650	1.0000	-	+0.4350	-0.8700	109.47	-
SPC/Fw [2] [994]	a	3.166	0.650	1.0120	-	+0.410	-0.8200	113.24	-
TIP3P [180]	a	3.15061	0.6364	0.9572	-	+0.4170	-0.8340	104.52	-
TIP3P/Fw [2] [994]	a	3.1506	0.6368	0.9600	-	+0.4170	-0.8340	104.5	-
PPC [1, 2] [3]	b	3.23400	0.6000	0.9430	0.06	+0.5170	-1.0340	106.00	127.00
TIP4P [180]	c	3.15365	0.6480	0.9572	0.15	+0.5200	-1.0400	104.52	52.26
TIP4P-Ew [649]	c	3.16435	0.680946	0.9572	0.125	+0.52422	-1.04844	104.52	52.26
TIP4P-FQ [197]	c	3.15365	0.6480	0.9572	0.15	+0.63[1]	-1.26[1]	104.52	52.26
TIP4P/Ice [838]	c	3.1668	0.8822	0.9572	0.1577	+0.5897	-1.1794	104.52	52.26
TIP4P/2005 [984]	c	3.1589	0.7749	0.9572	0.1546	+0.5564	-1.1128	104.52	52.26
TIP4P/2005f [1765]	c	3.1644	0.7749	0.9664	0.15555	+0.5564	-1.1128	104.75	52.375
SWFLEX-AI [2] [201]	c	four terms used		0.968[1]	0.14[1,3]	+0.6213	-1.2459	102.7[1]	51.35[1]
COS/G3 [704] [9]	c	3.17459	0.9445	1.0000	0.15	+0.450672	-0.901344	109.47	-
COS/D [1617] [9] [16]	c	3.4365	0.5119	0.9572	0.257	+0.5863	-1.1726	104.52	-
GCPM [2] [859] [10]	c	3.69 [4,11]	0.9146 [4]	0.9572	0.27	+0.6113	-1.2226	104.52	52.26
SWM4-NDP [2] [13] [933]	c	3.18395	0.88257	0.9572	0.24034	0.55733	-1.11466	104.52	52.26
ST2 [872] [12]	d	3.10000	0.31694	1.0000	0.80	+0.24357	-0.24357	109.47	109.47
TIP5P [180]	d	3.12000	0.6694	0.9572	0.70	+0.2410	-0.2410	104.52	109.47
TIP5P-Ew [619]	d	3.097	0.7448	0.9572	0.70	+0.2410	-0.2410	104.52	109.47
TTM2-F [1027] [14]	c	five parameters used		0.9572	0.70	+0.574	-1.148	104.52	52.26
POL5/TZ [2] [256]	d	2.9837 [4]	4	0.9572	0.5	varies [5]	-0.42188	104.52	109.47
Six-site [491]	c/d[7]	3.115_{OO} 0.673_{HH}	0.715_{OO} 0.115_{HH}	0.980	0.8892_{L} 0.230_{M}	+0.477	-0.044_{L} -0.866_{M}	108.00	111.00
QCT [1251]	a[15]	3.140	0.753	0.9614	-	+0.6064	-1.2128	104.067	-

Water

- Best model? ⇒ B. Guillot. *A reappraisal of what we have learnt during three decades of computer simulations of water.* J.Mol. Liquids **101**, 219 (2002)

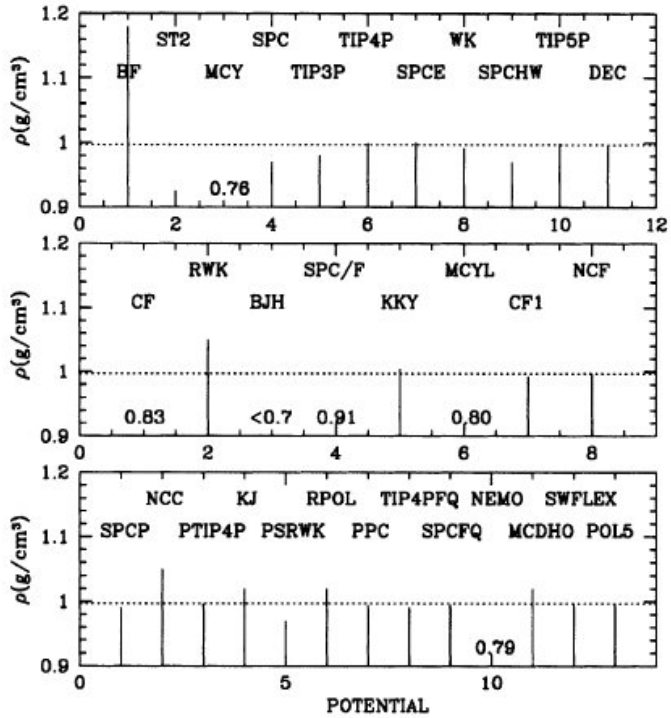
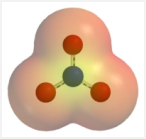


Figure 1. Density of simulated water at 298K and 1bar for different model potentials (see Table):top panel (rigid models), middle panel (flexible models) and bottom panel (polarizable models). The dotted line indicates the experimental value for H_2O (0.997g/cm3).



Pertubative treatment

- Perturbation theory

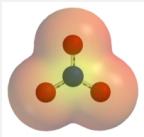
$$\hat{H} = \hat{H}^{(0)} + \lambda \hat{H}' \Rightarrow \begin{cases} E = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \dots \\ \psi = \psi^{(0)} + \lambda \psi^{(1)} + \lambda^2 \psi^{(2)} + \dots \end{cases}$$

$$E^{(i)}, \psi^{(i)} \Rightarrow \langle \psi_i^{(0)} | H' | \psi_j^{(0)} \rangle$$

$$\downarrow$$

analytical/numerical

- Analytical expresions $\Rightarrow$ cumbersome
- Convergence properties
- Useful for interpretation



Variational method

- Linear variational method

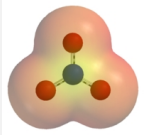
$$\hat{H} = \hat{H}^{(0)} + \hat{H}' \Rightarrow \begin{cases} \hat{H}^{(0)}\psi^{(0)} = E^{(0)}\psi^{(0)} \rightarrow \text{ basis set} \\ \psi = \sum_k c_k \psi_k^{(0)} \end{cases}$$

$$\mathbf{C}^\dagger \mathbf{H} \mathbf{C} = \mathbf{\Lambda} \Rightarrow \langle \psi_i^{(0)} | H' | \psi_j^{(0)} \rangle$$

$$\downarrow$$

analytical/numerical

- Diagonalization $\Rightarrow$ computationally demanding
- Convergence properties
- Choice of the basis set



DVR method

- Discrete Variable Representation method

$$\varphi_i^{(0)} \rightarrow \text{ HO, particle in a box,...}$$

$$\downarrow$$

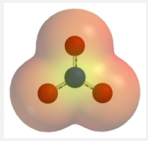
$$\langle \varphi_i^{(0)} | \hat{x} | \varphi_j^{(0)} \rangle \rightarrow \mathbf{B}^\dagger \mathbf{X} \mathbf{B} = \boldsymbol{\lambda}_x$$

$$\downarrow$$

$$\langle \phi_i^{\mathrm{DVR}} | \hat{x} | \phi_j^{\mathrm{DVR}} \rangle = \lambda_{x_i} \delta_{ij} \leftarrow \phi_i^{\mathrm{DVR}} = \sum_k b_{ki} \varphi_k^{(0)}$$

$$\downarrow$$

$$\langle \phi_i^{\mathrm{DVR}} | \hat{V}(x) | \phi_j^{\mathrm{DVR}} \rangle \approx V(\lambda_{x_i}) \delta_{ij}$$



DVR method

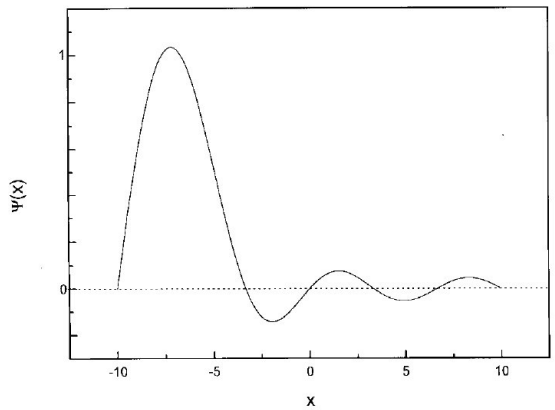


Figure 1A. Particle in a box DVR. The system is defined for a box ranging from - 10 to 10 bohr.

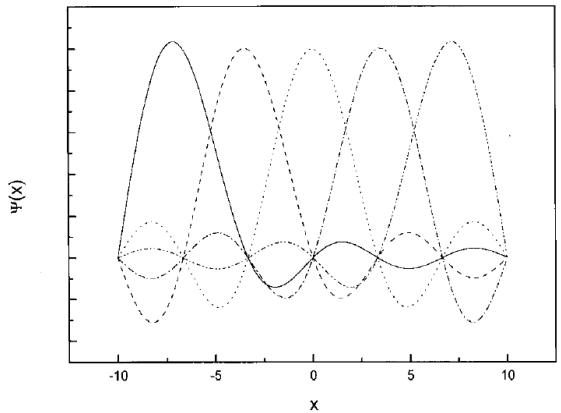


Figure 1B. A set of 5 particle in a box DVR's. The quadrature points are equaly spaced in this case.

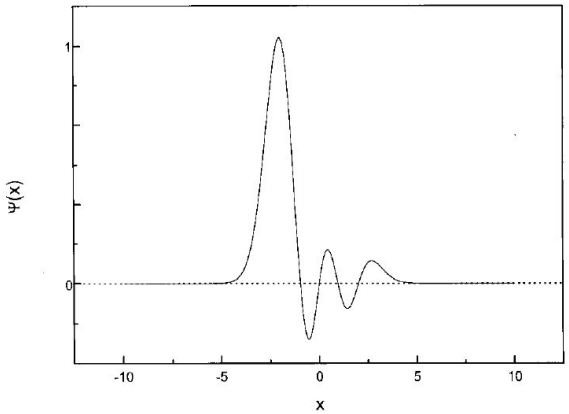


Figure 2A. A Numerically Generated DVR (NG-DVR) for the harmonic oscillator.

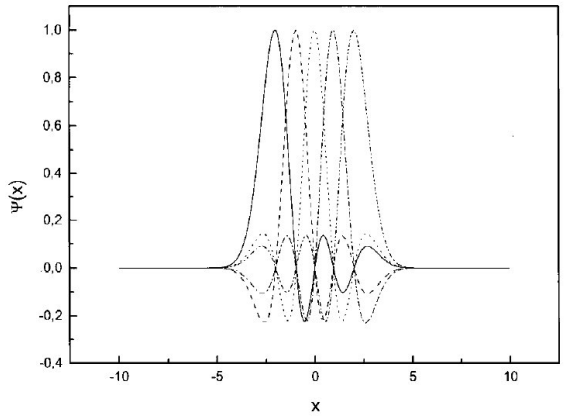


Figure 2B. A set of 5 NG-DVR for the harmonic oscillator.

J.J. Soares Neto and L.S. Costa, Braz. J. Phys. 28, 1 (1998)