Systèmes quantiques simples pour mieux comprendre la physique et chimie des systèmes complexes

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Seminaire SFP Midi-Pyrénées

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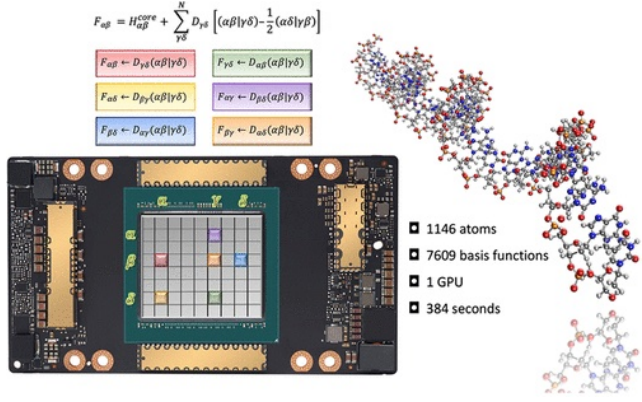
Why bother with electron correlation?

$$E_c = E_{\text{exact}} - \underbrace{E_{\text{Hartree-Fock}}}_{\text{mean-field}}$$

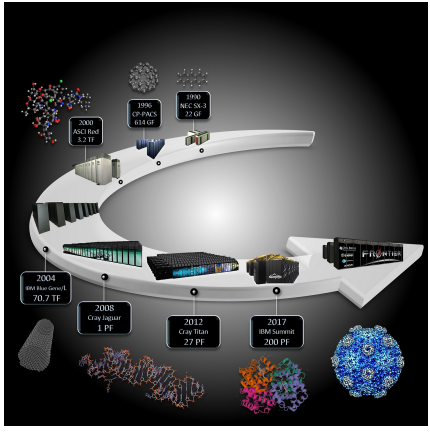
- ☺ Hartree-Fock theory ignores correlation and gives 99% of the energy
- ☺ It is often accurate for the prediction of molecular structures
- ☺ It is computationally cheap and can be applied to large systems
- ☹ Unfortunately, the final 1% can have important chemical effects
- ☹ This is particularly true when bonds are broken and/or formed
- ☹ Thus, realistic physics and chemistry requires a good treatment of correlation

Hartree-Fock calculation on a single GPU



Barca et al. JCTC 16 (2020) 7232

Hartree-Fock calculation on supercomputers



Barca et al. SC'20: Proceedings of the International Conference for High Performance Computing, Networking, Storage and Analysis 81 (2020) 1-14

Some random thoughts on electron correlation

- The concept was introduced at the dawn of electronic structure theory
  Wigner Phys Rev 46 (1934) 1002

- Its definition was agreed somewhat later
  Löwdin Adv Chem Phys 2 (1959) 207

☹ One Nobel Laureate used to refer to it as "the stupidity energy"
Feynmann (1972)

☺ There have been recent heroic calculations on the helium atom
Nakashima & Nakatsuji JCP 127 (2007) 224104

☹ "We conclude that theoretical understanding here lags well behind the power of available computing machinery"
Schwartz Int J Mod Phys E 15 (2006) 877

The helium-like ions: One nucleus of charge Z and Two electrons

The Hamiltonian operator (in atomic units $m = \hbar = e = 1$)

$$\hat{H} = -\frac{1}{2}\left(\nabla_1^2 + \nabla_2^2\right) - Z\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{1}{r_{12}} \quad \text{where} \quad r_{12} = |\boldsymbol{r}_1 - \boldsymbol{r}_2|$$

- $Z = 1$ gives the H^- anion
- $Z = 2$ gives the He atom
- $Z = 3$ gives the Li^+ cation
- $Z = 4$ gives the Be^{2+} cation
- etc.

History of accurate (non-relativistic) calculation on the He atom

"For thousands of years mathematicians have enjoyed competing with one other to compute ever more digits of the number π. Among modern physicists, a close analogy is computation of the ground state energy of the helium atom, begun 75 years ago by E. A. Hylleraas."

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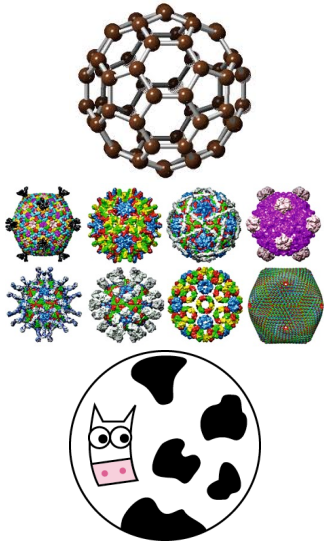
The "spherium" model: Why bother with electron(s) on a sphere?



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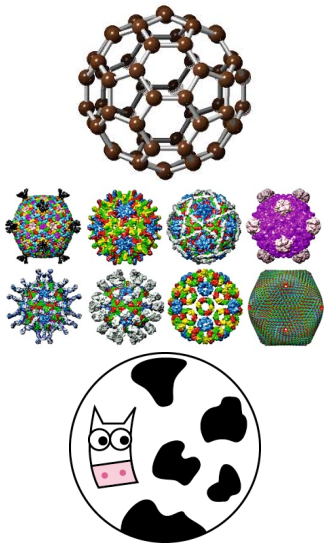
Arguments for high-impact journals

It can be experimentally realized:

- Multielectron bubbles in liquid helium
- Arrangements of protein subunits on spherical viruses
- Colloid particles in colloidosomes
- Fullerene-like molecules: C_{60}, C_{240}, C_{540}, ...



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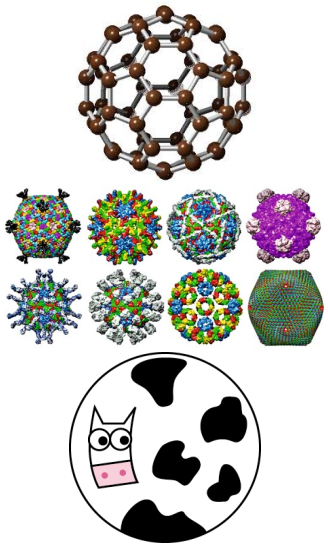
Other arguments...

- It yielded a number of unexpected discoveries
- This is actually related to "real" Physics and Chemistry



The spherium atom: electron(s) on a sphere of radius R

Loos & Gill PRA 79 (2009) 062517

One electron on a sphere

$$\hat{H} = -\frac{1}{2}\nabla^2$$

Solution:

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Solution:
??? $\Rightarrow$ Exciting!!!

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$R = 1,$ $\quad E_{\mathrm{Sp}} = 0.852\ 781\ 065\ 056\ 462\ 665\ 400\ 437\ 966\ 038\ 710\ 264\ \ldots$
$R = 100,$ $\quad E_{\mathrm{Sp}} = 0.005\ 487\ 412\ 426\ 784\ 081\ 726\ 642\ 485\ 484\ 213\ 968\ \ldots$

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Observation:

— With a small expansion $\psi = \sum_k c_k r_{12}^k$, one can get many digits! —

Is it trying to tell us something?
Loos & Gill PRA 79 (2009) 062517

Hamiltonian of the ground state

$$\hat{H} = \left(\frac{r_{12}^2}{4R^2} - 1 \right) \frac{d^2}{dr_{12}^2} + \left(\frac{3r_{12}}{4R^2} - \frac{1}{r_{12}} \right) \frac{d}{dr_{12}} + \frac{1}{r_{12}}$$

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Frobenius method

We seek polynomial solutions $\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = \sum_{\ell=0}^{\infty} c_\ell r_{12}^\ell$ and we get $c_{\ell+2} = \dfrac{c_{\ell+1} + [\ell(\ell+2)/(4R^2) - E]c_\ell}{(\ell+2)^2}$

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Analytical solutions

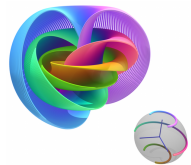
$R = \sqrt{3}/2$	$E = 1$	$\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = 1 + r_{12}$
$R = \sqrt{7}$	$E = 2/7$	$\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = 1 + r_{12} + \frac{5}{28} r_{12}^2$
$\vdots$	$\vdots$	$\vdots$

Loos & Gill PRL 103 (2009) 123008

The glomium atom: electron(s) on a glome

What is a "glome"?

A glome is a 3-sphere, i.e. the surface of a 4-dimensional ball



$$\hat{H} = \left(\frac{r_{12}^2}{4R^2} - 1\right)\frac{d^2}{dr_{12}^2} + \left(\frac{5r_{12}}{4R^2} - \frac{2}{r_{12}}\right)\frac{d}{dr_{12}} + \frac{1}{r_{12}}$$

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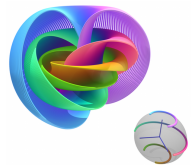

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Analytical solutions

$R = \sqrt{10}/2 \quad E = 1/2 \quad \Psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = 1 + \frac{1}{2} r_{12}$

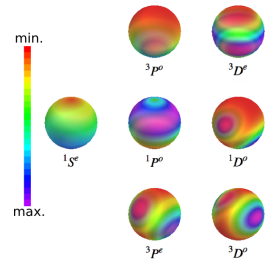
$R = \sqrt{66}/2 \quad E = 2/11 \quad \Psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = 1 + \frac{1}{2} r_{12} + \frac{7}{132} r_{12}^2$

$\vdots \qquad \vdots \qquad \vdots$

Simplest exact solutions for a D-sphere

D	$4R^2$	E	$\Psi(r_1, r_2)$
1	6	$2/3$	$r_{12}(1 + r_{12}/2)$
2	3	1	$1 + r_{12}$
3	10	$1/2$	$1 + r_{12}/2$
4	21	$1/3$	$1 + r_{12}/3$
$\vdots$	$\vdots$	$\vdots$	$\vdots$
D	$(2D-1)(D-1)$	$1/(D-1)$	$1 + r_{12}/(D-1)$
$\vdots$	$\vdots$	$\vdots$	$\vdots$

— Kato's cusp conditions are identical to real systems —



Loos & Gill PRL 103 (2009) 123008; Mol Phys 108 (2010) 2527

What happen when an electron and a nucleus meet each other?

$$\hat{H}\psi = E\psi$$

$$\left(-\frac{\nabla^2}{2} + \hat{V}\right)\psi = E\psi$$

$$-\frac{1}{2}\left(\frac{d^2\psi}{dr^2} + \frac{2}{r}\frac{d\psi}{dr}\right) - \frac{Z}{r} = E\psi$$

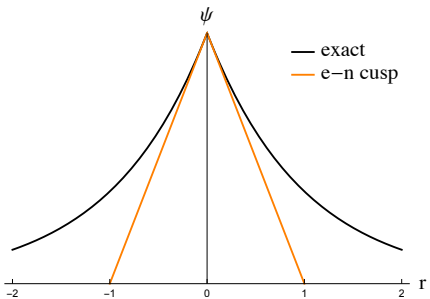
For small r, let's approximate the wave function as

$$\psi = 1 + \alpha r + O(r^2)$$

Then,

$$\alpha = -Z \quad \Rightarrow \quad \boxed{\psi \sim 1 - Zr \text{ for small } r}$$

Hydrogen atom ($Z = 1$):



This is the electron-nucleus (e-Z) cusp!

Kato, Com Pure Appl Math 10 (1957) 151; Pack and Byers Brown, JCP 45 (1966) 556

What happen when two electrons meet each other?

$$\nabla^2 = \frac{\partial^2}{\partial r_1^2} + \frac{2}{r_1}\frac{\partial}{\partial r_1} + \frac{\partial^2}{\partial r_2^2} + \frac{2}{r_2}\frac{\partial}{\partial r_2} + \frac{\partial^2}{\partial r_{12}^2} + \frac{4}{r_{12}}\frac{\partial}{\partial r_{12}} + \frac{r_1^2 + r_{12}^2 - r_2^2}{2r_1 r_{12}}\frac{\partial^2}{\partial r_1 \partial r_{12}} + \frac{r_2^2 + r_{12}^2 - r_1^2}{2r_2 r_{12}}\frac{\partial^2}{\partial r_2 \partial r_{12}}$$

$$\hat{V} = -\frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}$$

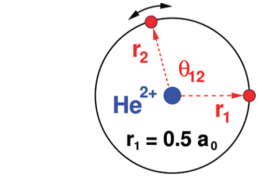
Let's assume r_{12} is tiny compared to r_1 and r_2

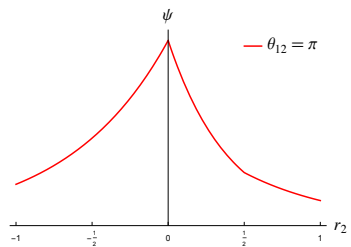
$$\psi = 1 + \beta r_{12}$$

Then,

$$\beta = \frac{1}{2} \quad \Rightarrow \quad \boxed{\psi \sim 1 + \frac{r_{12}}{2} \text{ for small } r_{12}}$$

This is the electron-electron (e-e) cusp!





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Ringium: "— *One Ring to Rule Them All* —"

Two Electrons on a Ring

Wavefunctions & Energies

$$\hat{H} = -\frac{1}{2R^2}\left[\frac{\partial^2}{\partial\theta_1^2} + \frac{\partial^2}{\partial\theta_2^2}\right] + \frac{1}{r_{12}}$$

$$E = ?$$

$$\Psi = ?$$

Separating the Hamiltonian

Let's define the extracule $\Theta = (\theta_1 + \theta_2)/2$ and intracule $\theta = \theta_1 - \theta_2$

Using these coordinates, the Hamiltonian is a sum of two independent parts

$$\hat{H} = -\frac{1}{4R^2}\frac{\partial^2}{\partial\Theta^2} - \frac{1}{R^2}\frac{\partial^2}{\partial\theta^2} + \frac{1}{2R\sin(\theta/2)}$$

so we can solve for the extracule and intracule wavefunctions separately.

$$-\frac{1}{4R^2}\frac{d^2}{d\Theta^2}\phi_J = \mathcal{E}_J\phi_J \qquad \left[-\frac{1}{R^2}\frac{d^2}{d\theta^2} + \frac{1}{2R\sin(\theta/2)}\right]\psi_j = \varepsilon_j\psi_j$$

The total wavefunctions and energies are then given by

$$\Psi_{Jj} = \phi_J(\Theta)\psi_j(\theta) \qquad E_{Jj} = \mathcal{E}_J + \varepsilon_j$$

Extracule Schrödinger equation

The Schrödinger equation for the extracule $\Theta = (\theta_1 + \theta_2)/2$ is

$$\boxed{-\frac{1}{4R^2}\frac{d^2}{d\Theta^2}\phi_J = \mathcal{E}_J\phi_J}$$

The resulting wavefunctions and energies are

$$\phi_J = \exp(\imath J\Theta) \qquad\qquad \mathcal{E}_J = \frac{J^2}{4R^2}$$

J	0	1	2	3	4	$\cdots$
Symmetry	Σ	Π	Δ	Φ	Γ	$\cdots$

Intracule Schrödinger equation

The Schrödinger equation for the intracule $\theta = \theta_1 - \theta_2$ is

$$\boxed{\left[-\frac{1}{R^2}\frac{d^2}{d\theta^2} + \frac{1}{2R\sin(\theta/2)} \right] \psi = \varepsilon\ \psi}$$

If we use the distance $u = |\boldsymbol{r}_1 - \boldsymbol{r}_2|$, instead of θ, we obtain the Heun-type differential equation

$$\left[\left(\frac{u^2}{4R^2} - 1 \right) \frac{d^2}{du^2} + \frac{u}{4R^2}\frac{d}{du} + \frac{1}{u} \right] \psi = \varepsilon\ \psi$$

If we define $x = u/(2R)$, the general solution is

$$\psi = x\ (1+x)^{a/2}\ (1-x)^{b/2}\ P(x)$$

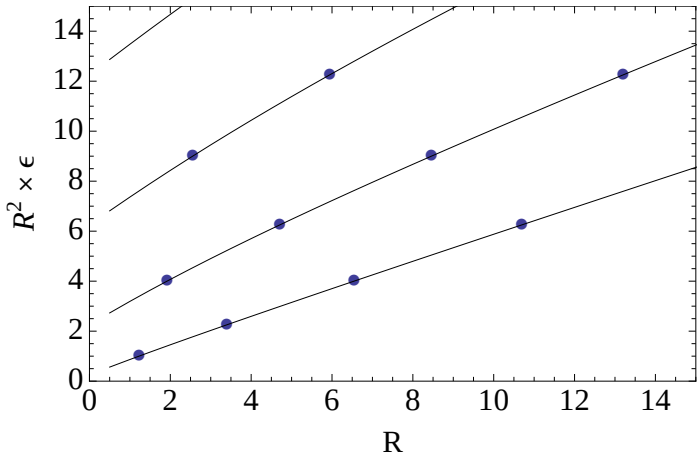
where $a = 0$ or 1, and $b = 0$ or 1, and $P(x)$ is a regular power series in x.

The four families of solutions

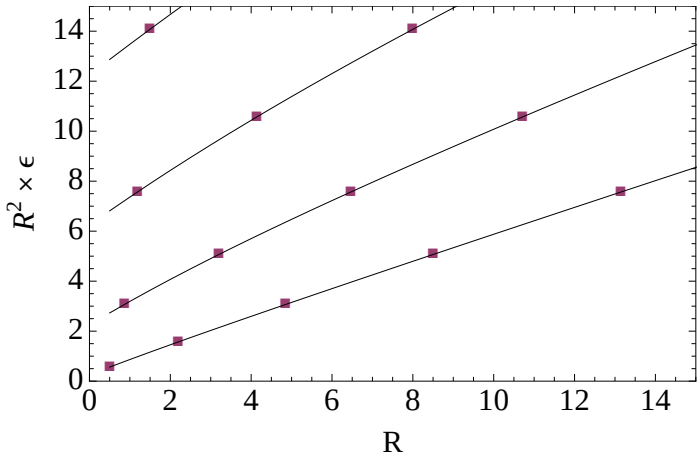
$$\psi = x\,(1+x)^{a/2}\,(1-x)^{b/2}\,P(x)$$

- Four families of solutions: $(a,b) = (0,0)$, $(1,0)$, $(0,1)$ or $(1,1)$
- $b = 0$ yields the ground, 2nd-excited, 4th-excited, etc. states.
- $b = 1$ yields the 1st-excited, 3rd-excited, 5th-excited, etc. states.
- When R is an "eigenradius", $P(x)$ terminates, becoming a polynomial
- In these cases, both ψ and ε can be obtained in closed form
- There are a countably infinite number of these closed-form solutions

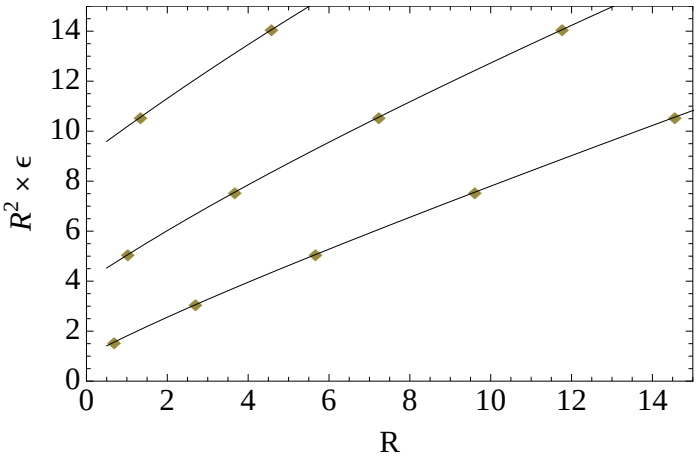
The $(a, b) = (0, 0)$ family



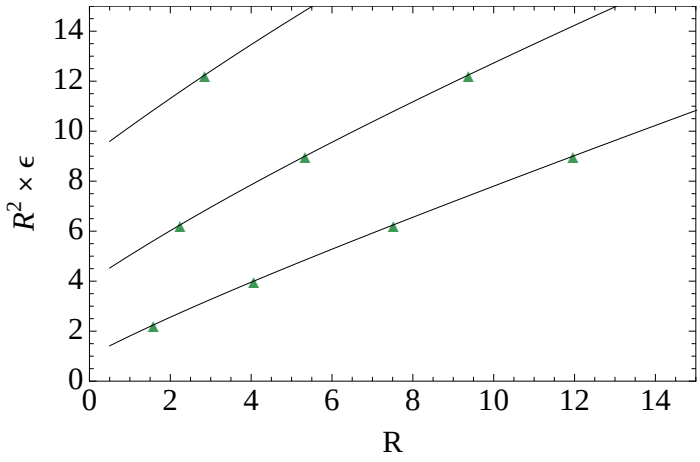
The $(a, b) = (1, 0)$ family

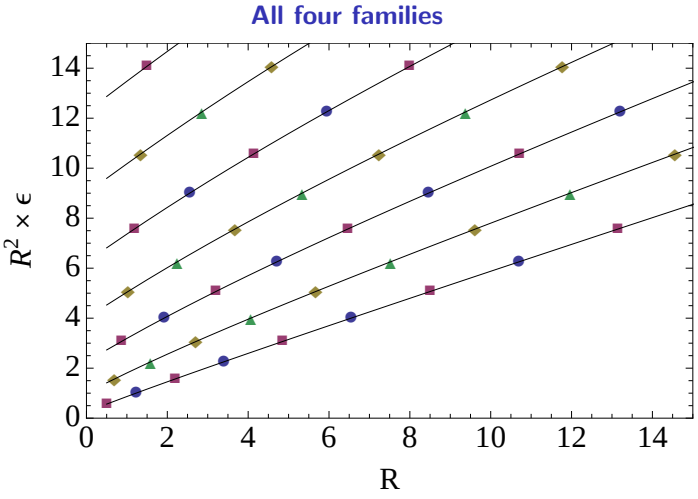


The $(a, b) = (0, 1)$ family



The $(a, b) = (1, 1)$ family



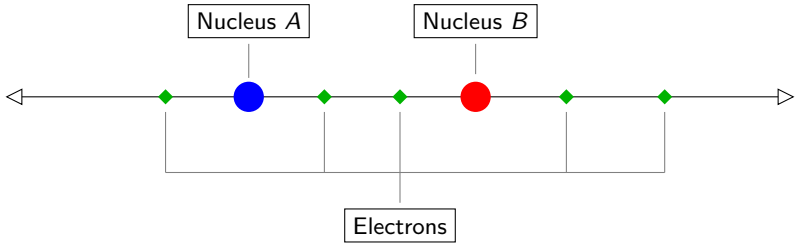

All four families
$R^2 \times \epsilon$
R
0
2
4
6
8
10
12
14

Some exact closed-form wavefunctions

State	R	ε	$\psi(u)$ $\quad x = u/(2R)$
Ground	$1/2$	$9/4$	$u\sqrt{1+x}$
	$\sqrt{3/2}$	$2/3$	$u\left[1+\frac{1}{2}u\right]$
	$\frac{1}{4}(\sqrt{33}+3)$	$\frac{25}{96}(7-\sqrt{33})$	$u\sqrt{1+x}\left[1+(R-\frac{1}{2})x\right]$
	$\sqrt{23/2}$	$9/46$	$u\left[1+\frac{1}{2}u+\frac{5}{2}x^2\right]$
⋮	⋮	⋮	⋮
1st excited	$\frac{1}{4}(\sqrt{33}-3)$	$\frac{25}{96}(7+\sqrt{33})$	$u\sqrt{1-x}\left[1+(R+\frac{1}{2})x\right]$
	$\sqrt{5/2}$	$9/10$	$u\sqrt{1-x}\sqrt{1+x}\left[1+\frac{1}{2}u\right]$
	$\sqrt{33/2}$	$8/33$	$u\sqrt{1-x}\sqrt{1+x}\left[1+\frac{1}{2}u+\frac{7}{2}x^2\right]$
⋮	⋮	⋮	⋮

Loos & Gill PRL 108 (2012) 083002

What is one-dimensional Chemistry?



Loos, Ball & Gill, PCCP 17 (2015) 3196
Ball, Loos & Gill, PCCP 19 (2017) 3987

Why one dimension?

Experimental

- Carbon nanotubes
- Atomic or semi-conducting nanowires (quantum wires)
- (very) Strong magnetic fields
- Many others!

Theoretical

- Test/Model system for electron behaviour and electronic correlation
- Lower dimensionality is simpler mathematically
- Dimensional reduction:

$$\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_n) \longrightarrow \Psi(x_1, x_2, \ldots, x_n)$$
$$\rho(x, y, z) \longrightarrow \rho(x)$$

Pecularities of 1D

- The Coulomb operator $|x|^{-1}$ is strongly *singular* in 1D
- This prevents us from solving the Schrödinger equation using normal techniques

Loudon [Am J Phys 27 (1959) 649]

- Found a set of solutions for the hydrogen atom in 1D by examining a sequence of truncated Coulomb operators that approach the unmodified operator
- Concluded that the ground state has an *infinite* binding energy due to the electron 'falling' onto the nucleus

More recent work

- Chemists use softened Coulomb interactions $(x^2+1)^{-1/2}$ to model experimentally available systems Wagner et al, PCCP 14 (2012) 8581
- Physicists argue over whether or not there is an infinite binding energy

Oliveira & Verri (2009 – 2012) and our work [PRL 108 (2012) 083002]

- There are an *infinite* number of treatments that work around the Coulomb singularity
- **But** the Dirichlet boundary conditions is the one to use:

$$\boxed{\Rightarrow \text{If } x_i = x_j \text{ or } x_i = x_A \text{ then } \Psi = 0}$$

Consequences of the Dirichlet boundary conditions

(1) Spin-blindness

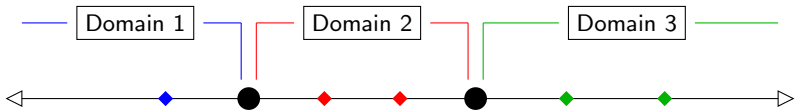
The energy of the system is invariant under any change of spin coordinates. As a result we can ignore the spin coordinates.

(2) Super-Pauli principle

Two electrons confined to one dimension cannot occupy the same quantum state regardless of spin. That is, only one electron may occupy each orbital.

(3) Nuclear impenetrability

Electrons are unable to pass from one side of a nucleus to another, and no tunnelling can occur in 1D systems. This separates space into regions that electrons become trapped within.



Notation

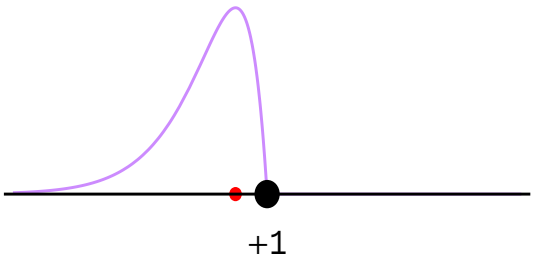
We use a special notation for 1D molecules to account for electrons occupying different domains.

Examples:

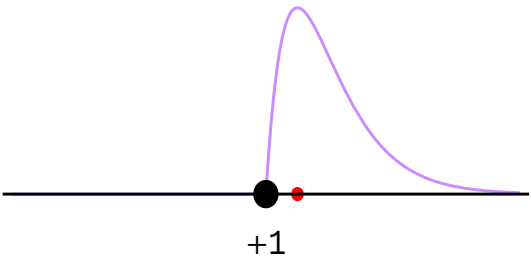
$${}_1H_2Li_1 \qquad {}_1H_1Li_2 \qquad {}_1He_3B_3H_1 \qquad H_3B_3$$

"Chirality" in 1D: Hydrogen atom

Left-handed ground state: $_1H$

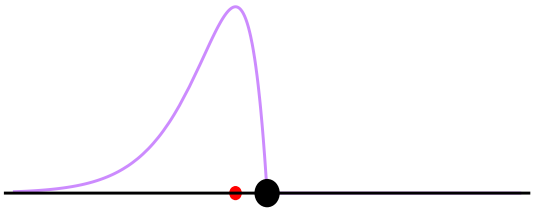


Right-handed ground state: H_1



"Chirality" in 1D: Hydrogen atom

Left-handed ground state: $_1\mathbf{H}$

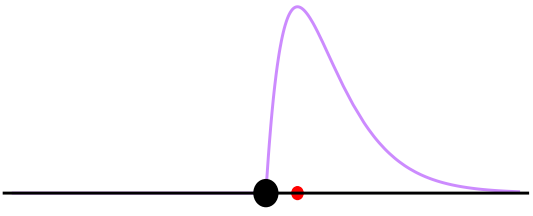


$$\psi(x) = -x\exp(+x)$$

$$E = -0.5$$

$$\mu = +1.5 \qquad R = \sqrt{\langle x^2 \rangle} = 1.8$$

Right-handed ground state: $\mathbf{H}_1$



$$\psi(x) = x\exp(-x)$$

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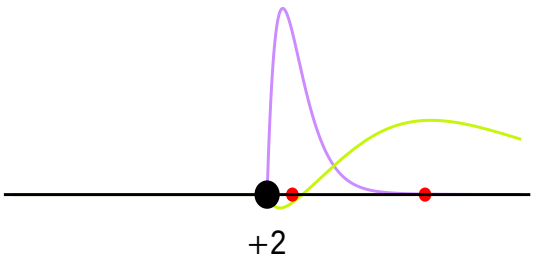
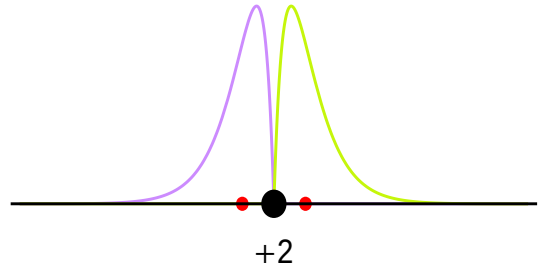
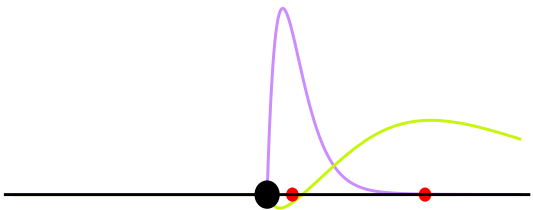
One-sided helium: $\mathrm{He}_{1,2}$



Two-sided helium: ${}_1\mathrm{He}_1$



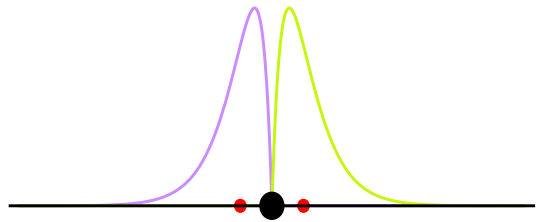
One-sided helium: $\mathrm{He}_{1,2}$



$E = -2.1074$

$\mu = +3.5 \qquad R = 4.8$

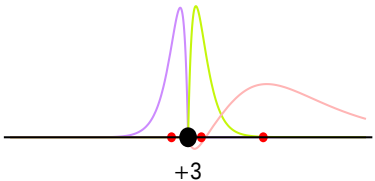
Two-sided helium: ${}_1\mathrm{He}_1$



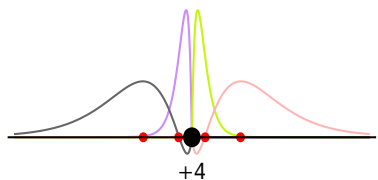
$E = -3.2429$

$\mu = 0 \qquad R = 1.0$

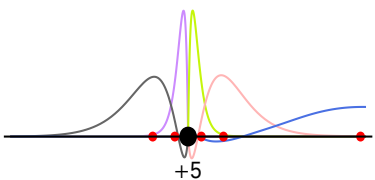
Lithium: $\mu = 1.5$ **and** $R = 2.8$



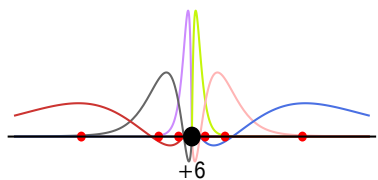
Beryllium: $\mu = 0$ **and** $R = 2.1$



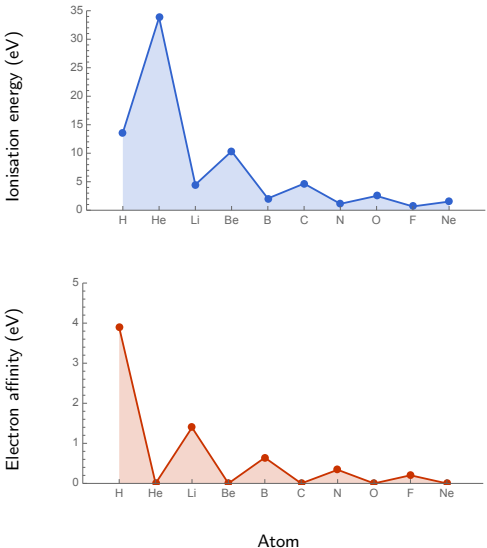
Boron: $\mu = 1.9$ **and** $R = 4.7$



Carbon: $\mu = 0$ **and** $R = 3.7$

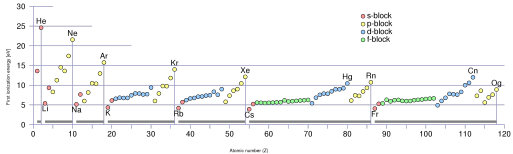


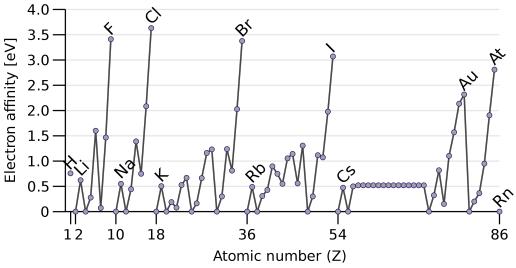
Ionisation energies and electron affinities (in eV)



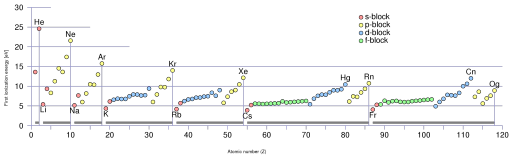
Atom	Ionisation energies	Electron affinities
H	13.606	3.893
He	33.822	—
Li	4.486	1.395
Be	10.348	—
B	2.068	0.643
C	4.670	—
N	1.125	0.340
O	2.515	—
F	0.666	0.203
Ne	1.518	—

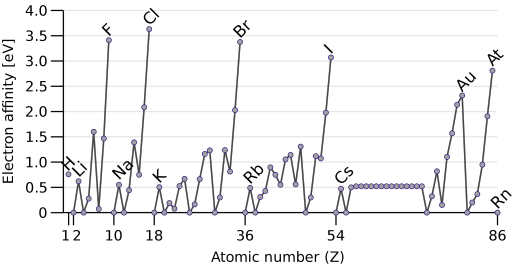
Ionization potentials and electron affinities in 3D

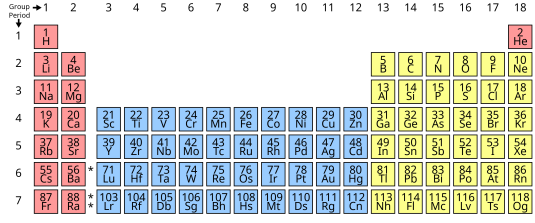




Ionization potentials and electron affinities in 3D







Periodic trends in 1D atoms

- 1D atoms have only two sides
- Shells hold only two electrons

- Odd electron $\Rightarrow$ unfilled shell
- Even electron $\Rightarrow$ filled shell

- Odd electron $\Rightarrow$ reactive
- Even electron $\Rightarrow$ unreactive

- Odd electron $\Rightarrow$ "alkali metals"
- Even electron $\Rightarrow$ "noble gases"

The 1D periodic table

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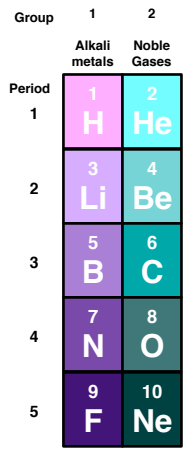
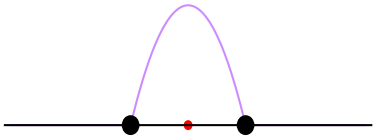
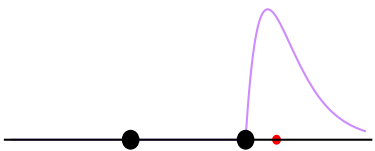
The 1D periodic table



The H_1H^+ state: $\mu = 0$

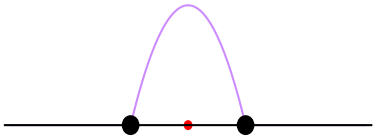


The HH_1^+ state: $\mu \neq 0$

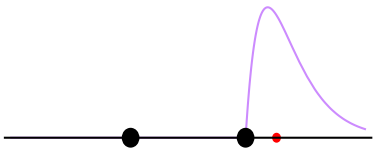


The H_2^+ molecule in 1D

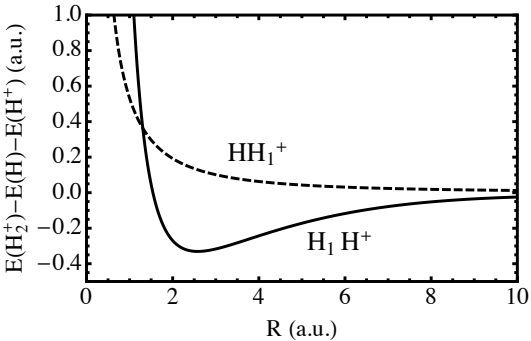
The H_1H^+ state: $\mu = 0$



The HH_1^+ state: $\mu \neq 0$

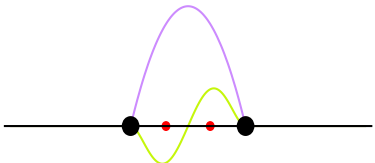


Potential energy curves for H_2^+

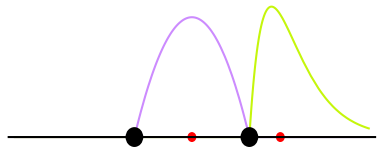


The H_2 molecule in 1D

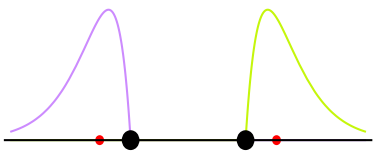
The H_2H state



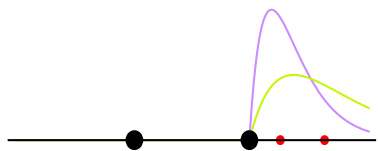
The H_1H_1 state



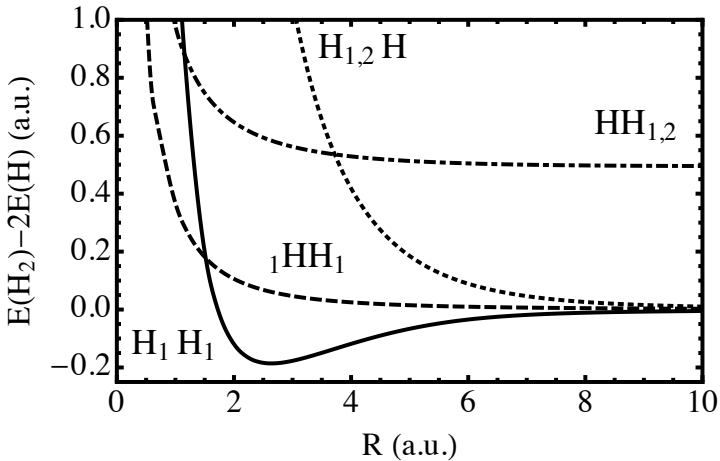
The $_1HH_1$ state



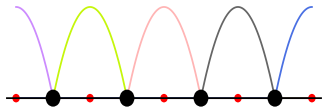
The HH_2 state



Potential energy curves for the H_2 molecule



Lego-style formation of 1D polymers



- A single H_1 atom has a dipole moment

⇒ Two H_1 atoms will feel dipole-dipole attraction

$$H_1 + H_1 \longrightarrow H_1H_1$$

- The resulting H_1H_1 molecule also has a dipole moment

⇒ H_1H_1 and H_1 will feel dipole-dipole attraction

$$H_1H_1 + H_1 \longrightarrow H_1H_1H_1$$

- The resulting $H_1H_1H_1$ molecule also has a dipole moment

⇒ $H_1H_1H_1$ and H_1 will feel dipole-dipole attraction

$$H_1H_1H_1 + H_1 \longrightarrow H_1H_1H_1H_1$$

Thank you!