One-dimensional Chemistry

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NZ Institute of Chemistry Conference, Queenstown

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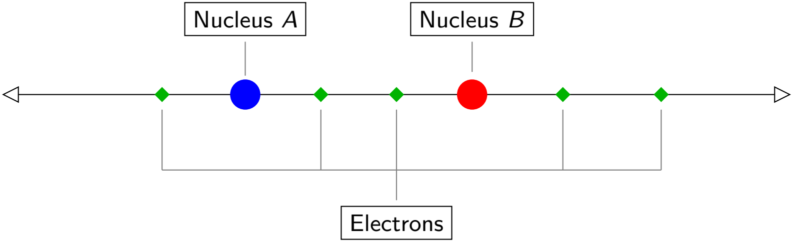
What is one-dimensional Chemistry?



Loos, Ball & Gill, PCCP 17 (2015) 3196
Ball, Loos & Gill, PCCP (submitted)

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:

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

Complications

Peculiarities 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

Way around it

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.

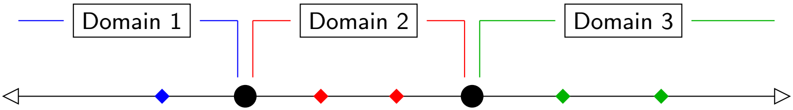
2 Super-Pauli principle

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



Notation

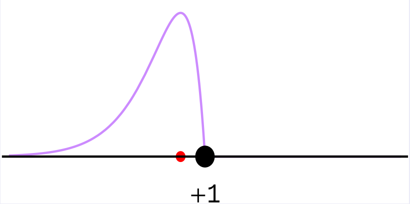
We use a special notation for 1D molecules to account for electrons occupying different domains.

Examples:

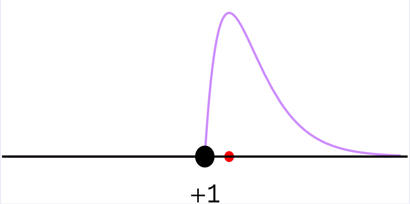
$_1H_2Li_1$ $_1H_1Li_2$ $_1He_3B_3H_1$ H_3B_3

“Chirality” in 1D: Hydrogen atom

Left-handed ground state: $_1H$



Right-handed ground state: H_1



"Chirality" in 1D: Hydrogen atom

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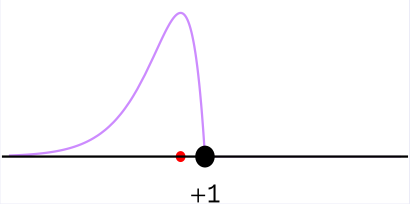
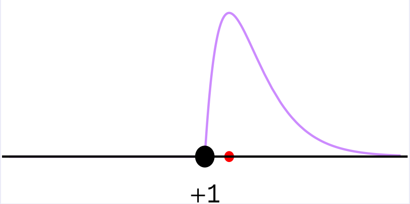


$$\psi(x) = -x \exp(+x)$$

$$E = -0.5$$

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

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



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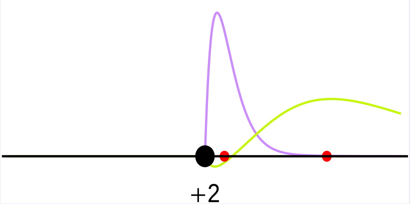
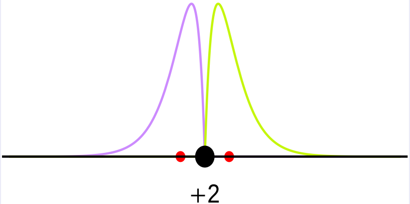
Helium atom in 1D

One-sided helium: $He_{1,2}$



Two-sided helium: ${}_1He_1$



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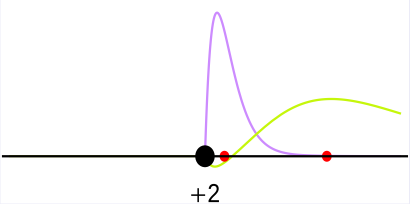
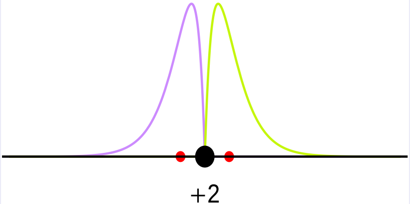


$$E = -2.1074$$

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

Two-sided helium: ${}_1He_1$

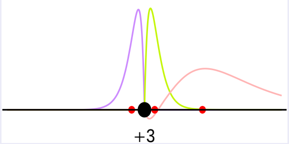


$$E = -3.2429$$

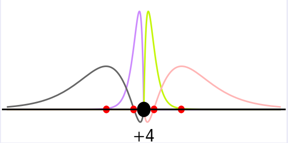
$$\mu = 0 \qquad R = 1.0$$

More 1D atoms...

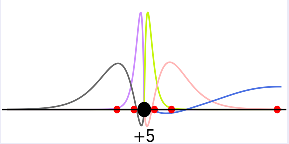
Lithium: $\mu = 1.5$ **and** $R = 2.8$



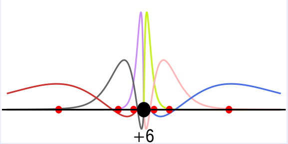
Beryllium: $\mu = 0$ **and** $R = 2.1$



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



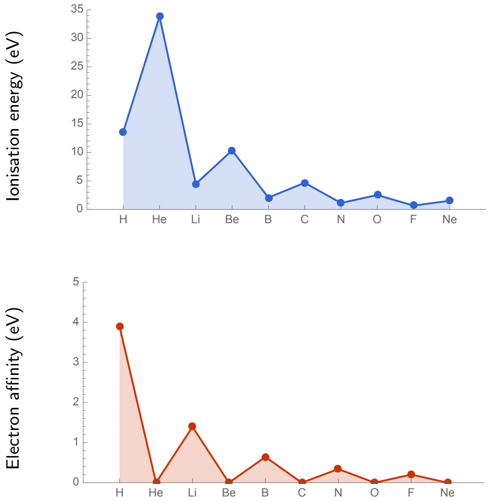
Carbon: $\mu = 0$ **and** $R = 3.7$



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	—

The periodic table in 1D



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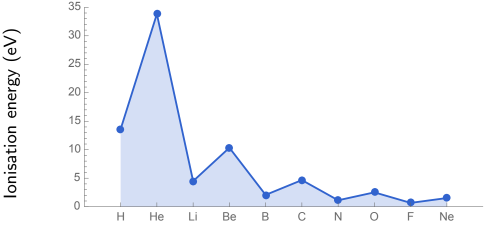
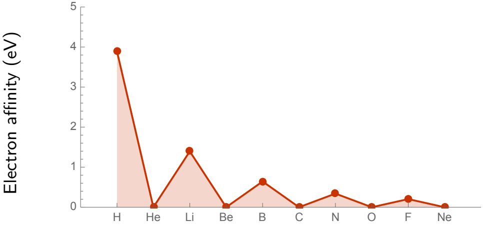
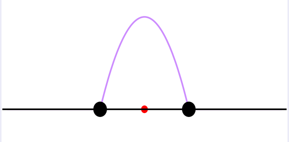




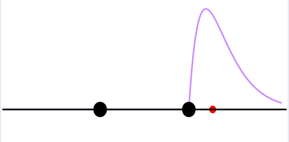
Group	1	2
	Alkali metals	**Noble Gases**
Period 1	1 H	2 He
2	3 Li	4 Be
3	5 B	6 C
4	7 N	8 O
5	9 F	10 Ne

The $H_2{}^+$ molecule in 1D

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



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



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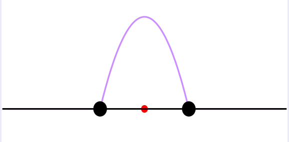

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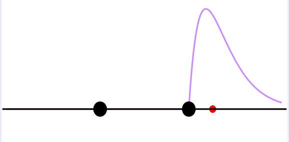
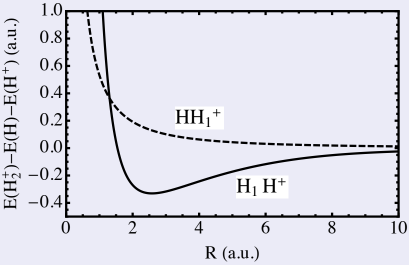
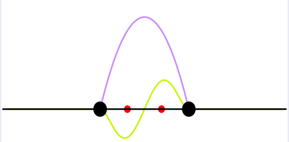


Potential energy curves for H_2^+

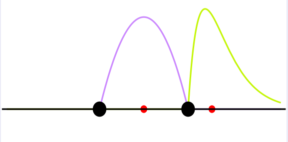


The H_2 molecule in 1D

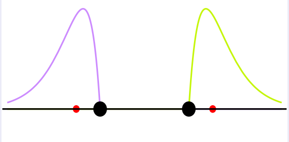
The H_2H state



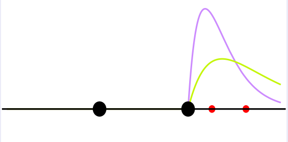
The H_1H_1 state



The ${}_1HH_1$ state

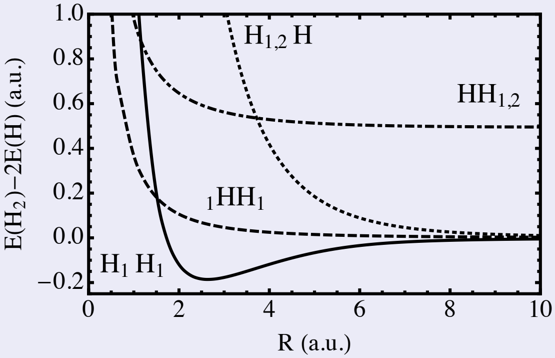


The HH_2 state

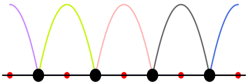


Two-electron diatomic molecules in 1D

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

$$H_1H_1H_1 + H_1 \longrightarrow H_1H_1H_1H_1$$

Collaborators and Funding

- Collaborators:

Caleb Ball

Peter Gill

- Research School of Chemistry & Australian National University
- Australian Research Council:
  Discovery Early Career Researcher Award 2013 & Discovery Project 2014

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