A mathematical picture of basic aspects of the periodic table

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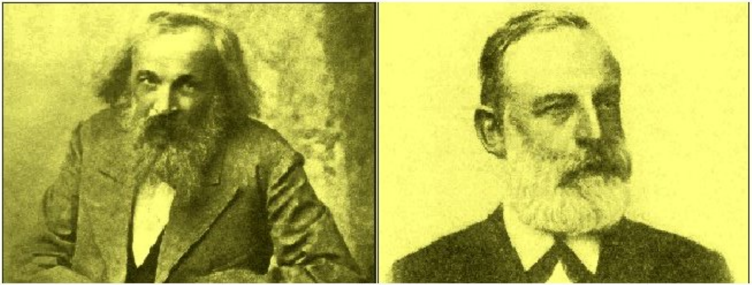
Joint work with Ben Goddard (Warwick)

Main reason why quantum mechanics (QM) is used in materials science and molecular modelling: it is chemically specific.

But rigorous mathematical work on QM to date has focused overwhelmingly on universal properties.

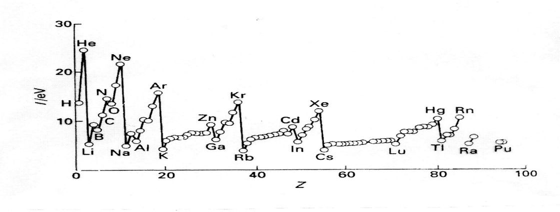
Goal: Begin to understand basic chemically specific properties of atoms mathematically from the Schrödinger equation.



1869: Periodic table of Lothar Meyer, Dimitri Mendelejew

Atoms can be grouped into a "periodic table", due to striking near-periodicities in physical and chemical behaviour

Example: Ionization energy as a function of atomic number (experiment)



1920s: Quantum mechanical explanation of Bohr, Hund, Slater

Chemical differences should come from different atoms having different electronic structure. Propose semi-empirical hydrogen orbital configurations

This talk:

Try to understand how some basic chemical differences between atoms emerge mathematically from the Schrödinger equation.

Schrödinger equation for atoms/ions

- N electrons, one nucleus of charge Z (neutral atoms: N=Z)
- Electronic strcture described by $\Psi : (\mathbb{R}^3 \times \mathbb{Z}_2)^N \to \mathbb{C}$
- Governing PDE: $\underbrace{\left(-\frac{1}{2}\Delta + V(x)\right)}_{=:H}\Psi = E\Psi$
- Potential: Coulomb attraction of electrons by nucleus, Coulomb repulsion between electrons

$$V(x) = -\sum_{i=1}^{N} \frac{Z}{|x_i|} + \sum_{1\le i<j\le N} \frac{1}{|x_i - x_j|}$$

- Antisymmetry condition:

$$\Psi(.., x_i, s_i, .., x_j, x_j, ..) = -\Psi(.., x_j, s_j, .., x_i, s_i, ..)$$

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SE for single Carbon atom (N=6) is a PDE in $\mathbb{R}^{3N} = \mathbb{R}^{18}$.

Discretize: $\mathbb{R} \to 10$ gridpoints $\Longrightarrow \mathbb{R}^{3N} \to 10^{18}$ gridpoints.

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3. Key ingredient for understanding chemistry: nodes
Competition between $-\Delta + V(x)$ (wants positive ground state), antisymmetry (forces more and more nodes as N increases), spin (allows to avoid some nodes), and electrostatic details of $V(x)$ (influences where the nodes go).

Without antisymmetry, every element would be like Hydrogen. Without spin, hydrogen would be like Helium, Helium like Beryllium, Beryllium like some sort of Carbon. Either way, all hell would break loose.

Function space for the Schrödinger equation

Kato's theorem: H is a self-adjoint, bounded below operator on $L^2_{anti}((\mathbb{R}^3 \times \mathbb{Z}_2)^N)$ with domain $H^2_{anti}((\mathbb{R}^3 \times \mathbb{Z}_2)^N)$.

Mathematical definition of basic chemical quantities

Energy level := eigenvalue of $H=-\frac{1}{2}\Delta+V(x)$

Zhislin's thm: For $N \leq Z$ (neutral atoms and positive ions), there exist exactly countably many eigenvalues, the corresponding eigenspaces being finite-dimensional. Variational pf: GF, ARMA, 2003

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Ground state spin and angular momentum quantum numbers

$L \in \{0,1,2,3,...\}$, $S \in \{0,\frac{1}{2},1,\frac{3}{2},...\}$
They measure the amount of symmetry of the functions in the GS under spatial and spin rotation. Of crucial chemical importance. Zero if and only if the functions in the GS are invariant.

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SE for atoms and its domain invariant under SO(3)$\times$SU(2)$\times\mathbb{Z}_2$

(i) simultaneous rotation of all electron positions about the origin, $\Psi(x_1, s_1, .., x_N, s_N) \mapsto \Psi(R^T x_1, s_1, .., R^T x_N, s_N)$, $R \in SO(3)$

(ii) simultaneous rotation of all electron spins (by $U \in SU(2)$)

(iii) simultaneous inversion of all electron positions at the origin.

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Conserved quantities (op's which commute with Hamiltonian):

(i) $\underline{L} = \frac{1}{i} \sum_{j=1}^{N} x_j \wedge \nabla_{x_j}$ many-el.ang.mom.operator

(ii) $\underline{S}$ many-electron spin operator

(iii) P parity operator

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Representation theory for Lie algebra of symmetry group gives:

- $\underline{L}^2$, $\underline{L}_3$, $\underline{S}^2$, $\underline{S}_3$, P commute with H and each other,
- the eigenvalues of $\underline{L}^2$ are L(L+1), L=0,1,2,...,
- on any irreducible e-space of H, $\underline{L}^2$ has only one eigenvalue.

The integer L parametrizing this $\underline{L}^2$ eigenvalue is called the ang.mom.quantum number of the eigenspace.

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Only option left: $Z \to \infty$.
Our results are rigorous asymptotic results in this limit.

Results, 1: Spin and angular momentum quantum numbers

Theorem

(GF/Goddard) For $N = 1, .., 10$*, and sufficiently large* Z*, the angular momentum and spin quantum numbers, and the dimension, of the Schrödinger ground state are:*

Atom	H	He	Li	Be	B	C	N	O	F	Ne
$\sharp$ electrons	1	2	3	4	5	6	7	8	9	10
L	0	0	0	0	1	1	0	1	1	0
S	$\frac{1}{2}$	0	$\frac{1}{2}$	0	$\frac{1}{2}$	1	$\frac{3}{2}$	1	$\frac{1}{2}$	0
Chemist's notation	^2S	^1S	^2S	^1S	^2P	^3P	^4S	^3P	^2P	^1S
dim	2	1	2	1	6	9	4	9	6	1

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♯ *electrons*	1	2	3	4	5	6	7	8	9	10
L	0	0	0	0	1	1	0	1	1	0
S	$\frac{1}{2}$	0	$\frac{1}{2}$	0	$\frac{1}{2}$	1	$\frac{3}{2}$	1	$\frac{1}{2}$	0
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Open problem: prove that these numbers do not change as Z is decreased down to $Z = N$.

Results, 2: Ground states

Theorem

(GF/Goddard) For $N = 1, .., 10$*, and large* Z*, the Schrödinger ground state is asymptotic to the explicit vector space given on the next slide, in the sense that the projection operators* P_0*,* $\tilde{P}_0$ *onto these spaces satisfy* $\lim_{Z \to \infty} |||P_0 - \tilde{P}_0||| = 0$*, the norm being the operator norm on* L^2*.*

Atom	Symmetry	Ground state	Dimension
H	^2S	$\lvert 1\rangle$, $\lvert \bar{1}\rangle$	2
He	^1S	$\lvert 1\bar{1}\rangle$	1
Li	^2S	$\lvert 1\bar{1}2\rangle$, $\lvert 1\bar{1}\bar{2}\rangle$	2
Be	^1S	$\frac{1}{\sqrt{1+c^2}}\left(\lvert 1\bar{1}2\bar{2}\rangle + c\frac{1}{\sqrt{3}}(\lvert 1\bar{1}3\bar{3}\rangle + \lvert 1\bar{1}4\bar{4}\rangle + \lvert 1\bar{1}5\bar{5}\rangle)\right)$ $c = -\frac{\sqrt{3}}{59049}(2\sqrt{1509308377} - 69821) = -0.2310996\dots$	1
B	$^2P^o$	$\frac{1}{\sqrt{1+c^2}}\left(\lvert 1\bar{1}2\bar{2}i\rangle + c\frac{1}{\sqrt{2}}(\lvert 1\bar{1}ij\bar{j}\rangle + \lvert 1\bar{1}ik\bar{k}\rangle)\right)$ $\frac{1}{\sqrt{1+c^2}}\left(\lvert 1\bar{1}2\bar{2}\bar{i}\rangle + c\frac{1}{\sqrt{2}}(\lvert 1\bar{1}\bar{i}j\bar{j}\rangle + \lvert 1\bar{1}\bar{i}k\bar{k}\rangle)\right)$ $(i,j,k) = (3,4,5), (4,5,3), (5,3,4)$ $c = -\frac{\sqrt{2}}{393660}(\sqrt{733174301809} - 809747) = -0.1670823\dots$	6
C	^3P	$\frac{1}{\sqrt{1+c^2}}(\lvert 1\bar{1}2\bar{2}ij\rangle + c\lvert 1\bar{1}k\bar{k}ij\rangle)$ $\frac{1}{\sqrt{1+c^2}}\left(\frac{1}{\sqrt{2}}(\lvert 1\bar{1}2\bar{2}i\bar{j}\rangle + \lvert 1\bar{1}2\bar{2}\bar{i}j\rangle) + c\frac{1}{\sqrt{2}}(\lvert 1\bar{1}k\bar{k}i\bar{j}\rangle + \lvert 1\bar{1}k\bar{k}\bar{i}j\rangle)\right)$ $\frac{1}{\sqrt{1+c^2}}(\lvert 1\bar{1}2\bar{2}\bar{i}\bar{j}\rangle + c\lvert 1\bar{1}k\bar{k}\bar{i}\bar{j}\rangle)$ $(i,j,k) = (3,4,5), (4,5,3), (5,3,4)$ $c = -\frac{1}{98415}(\sqrt{221876564389} - 460642) = -0.1056318\dots$	9
N	$^4S^o$	$\lvert 1\bar{1}2\bar{2}345\rangle$ $\frac{1}{\sqrt{3}}(\lvert 1\bar{1}2\bar{2}\bar{3}45\rangle + \lvert 1\bar{1}2\bar{2}3\bar{4}5\rangle + \lvert 1\bar{1}2\bar{2}34\bar{5}\rangle)$ $\frac{1}{\sqrt{3}}(\lvert 1\bar{1}2\bar{2}\bar{3}\bar{4}5\rangle + \lvert 1\bar{1}2\bar{2}\bar{3}4\bar{5}\rangle + \lvert 1\bar{1}2\bar{2}3\bar{4}\bar{5}\rangle)$ $\lvert 1\bar{1}2\bar{2}\bar{3}\bar{4}\bar{5}\rangle$	4
O	^3P	$\lvert 1\bar{1}2\bar{2}i\bar{i}jk\rangle$ $\frac{1}{\sqrt{2}}(\lvert 1\bar{1}2\bar{2}i\bar{i}j\bar{k}\rangle + \lvert 1\bar{1}2\bar{2}i\bar{i}\bar{j}k\rangle)$ $\lvert 1\bar{1}2\bar{2}i\bar{i}\bar{j}\bar{k}\rangle$ $(i,j,k) = (3,4,5), (4,5,3), (5,3,4)$	9
F	$^2P^o$	$\lvert 1\bar{1}2\bar{2}i\bar{i}j\bar{j}k\rangle$ $\lvert 1\bar{1}2\bar{2}i\bar{i}j\bar{j}\bar{k}\rangle$ $(i,j,k) = (3,4,5), (4,5,3), (5,3,4)$	6
Ne	^1S	$\lvert 1\bar{1}2\bar{2}3\bar{3}4\bar{4}5\bar{5}\rangle$	1

Schrödinger ground states in the limit $Z \to \infty$.

Notation

Hypergeometric functions (low hydrogen eigenstates)

$\phi_{1s}(x) = \frac{Z^{3/2}}{\sqrt{\pi}} e^{-Z|x|}$, $\phi_{1s} : \mathbb{R}^3 \to \mathbb{C}$ (1s-orbital)

$\phi_{2s}(x) = \left(1 - \frac{Z|x|}{2}\right) e^{-Z|x|/2}$ (2s-orbital)

$\phi_{2p_i}(x) = \frac{Z^{5/2}}{\sqrt{32\pi}} x_i e^{-Z\frac{|x|}{2}}$, $i = 1, 2, 3$ (2p-orbital)

Spin functions

$\uparrow : \{\pm\frac{1}{2}\} \to \mathbb{C}$, $\uparrow(s) = \delta_{1/2}(s)$ (Spin-up-orbital)

$\downarrow : \{\pm\frac{1}{2}\} \to \mathbb{C}$, $\downarrow(s) = \delta_{-1/2}(s)$ (Spin-down-orbital)

Joint space/spin functions in $L^2(\mathbb{R}^3 \times \mathbb{Z}_2)$

$1, 2, 3, 4, 5 = \phi_{1s}\uparrow, \phi_{2s}\uparrow, \phi_{2p_3}\uparrow, \phi_{2p_1}\uparrow, \phi_{2p_2}\uparrow$, where

$(\phi_{1s}\uparrow)(x, s) = \phi_{1s}(x)\uparrow(s)$

$\overline{1}, \overline{2}, \overline{3}, \overline{4}, \overline{5}$ = same with spin down

Antisymmetrised tensor products, alias Slater determinants

(of N orthonormal functions $\psi_1, \ldots, \psi_N \in L^2(\mathbb{R}^3 \times \{\pm\frac{1}{2}\})$):

$$\Big|\psi_1 \ldots \psi_N\Big\rangle(x_1, s_1, \ldots, x_N, s_N) = \frac{1}{\sqrt{N!}} \det \begin{pmatrix} \psi_1(x_1, s_1) & \cdots & \psi_1(x_N, s_N) \\ \vdots & & \vdots \\ \psi_N(x_1, s_1) & \cdots & \psi_N(x_N, s_N) \end{pmatrix}$$

Results, 3: Excited states

Theorem

(GF/Goddard) Let $N = 1, .., 10$*, and let* $n(N)$ *be equal to, respectively, 1, 1, 2, 6, 8, 12, 8, 6, 2, 1.*

(i) For Z *suff. large, the lowest* $n(N)$ *Schrödinger energy levels* $E_1(N, Z) < ... < E_{n(N)}(N, Z)$ *have exactly the spin quantum no., angular momentum quantum number, and dimension given on the next slide.*

(ii) For $Z \to \infty$*, these energy levels have the asymptotic expansion*

$$\frac{E_j(N, Z)}{Z^2} = a^{(0)}(N) + \frac{1}{Z} a_j^{(1)} + O(\frac{1}{Z^2}),$$

with $a^{(0)}$, $a_j^{(1)}$ *as given on the next slide. Moreover all other energy levels are bounded away from* $a^{(0)}$ *as* $Z \to \infty$.

Also, have determined the asymptotic eigenspaces. A bit too complicated to record here.

	Symm.	Ψ	E	c	E (num.)	c (num.)
Li	^2S	Ψ_1	$-\frac{9}{8}Z^2+\frac{5965}{5832}Z$		-7.0566	
	$^2P^\circ$	Ψ_2	$-\frac{9}{8}Z^2+\frac{57397}{52488}Z$		-6.8444	
Be	^1S	$\frac{1}{\sqrt{1+c^2}}(\Psi_1+c\Psi_2)$	$-\frac{5}{4}Z^2+\frac{1}{1679616}(2813231-5\sqrt{1509308377})Z$	$-\frac{1}{59049}(2\sqrt{1509308377}-6981)\sqrt{3}$	-13.7629	-0.2311
	$^3P^\circ$	Ψ_4	$-\frac{5}{4}Z^2+\frac{1363969}{839808}Z$		-13.5034	
	$^1P^\circ$	Ψ_3	$-\frac{5}{4}Z^2+\frac{2826353}{1679616}Z$		-13.2690	
	^3P	Ψ_5	$-\frac{5}{4}Z^2+\frac{1449605}{839808}Z$		-13.0955	
	^1D	Ψ_6	$-\frac{5}{4}Z^2+\frac{14673197}{8398080}Z$		-13.0112	
	^1S	$\frac{1}{\sqrt{1+c^2}}(\Psi_1+c\Psi_2)$	$-\frac{5}{4}Z^2+\frac{1}{1679616}(2813231+5\sqrt{1509308377})Z$	$\frac{1}{59049}(2\sqrt{1509308377}+6981)\sqrt{3}$	-12.8377	4.3271
B	$^2P^\circ$	$\frac{1}{\sqrt{1+c^2}}(\Psi_3+c\Psi_4)$	$-\frac{11}{8}Z^2+\frac{1}{6718464}(16493659-\sqrt{733174301809})Z$	$-\frac{1}{393660}(\sqrt{733174301809}-809747)\sqrt{2}$	-22.7374	-0.1671
	^4P	Ψ_6	$-\frac{11}{8}Z^2+\frac{2006759}{839808}Z$		-22.4273	
	^2D	Ψ_7	$-\frac{11}{8}Z^2+\frac{40981549}{16796160}Z$		-22.1753	
	^2S	Ψ_1	$-\frac{11}{8}Z^2+\frac{4151299}{1679616}Z$		-22.0171	
	^2P	Ψ_5	$-\frac{11}{8}Z^2+\frac{8322281}{3359232}Z$		-21.9878	
	$^4S^\circ$	Ψ_2	$-\frac{11}{8}Z^2+\frac{706213}{279936}Z$		-21.7612	
	$^2D^\circ$	Ψ_8	$-\frac{11}{8}Z^2+\frac{14301407}{5598720}Z$		-21.6030	
	$^2P^\circ$	$\frac{1}{\sqrt{1+c^2}}(\Psi_3+c\Psi_4)$	$-\frac{11}{8}Z^2+\frac{1}{6718464}(16493659+\sqrt{733174301809})Z$	$\frac{1}{393660}(\sqrt{733174301809}+809747)\sqrt{2}$	-21.4629	5.9851
C	^3P	$\frac{1}{\sqrt{1+c^2}}(\Psi_6+c\Psi_7)$	$-\frac{3}{2}Z^2+\left(\frac{3806107}{1119744}-\frac{1}{3359232}\sqrt{221876564389}\right)Z$	$-\frac{1}{98415}(\sqrt{221876564389}-460642)$	-34.4468	-0.1056
	^1D	$\frac{1}{\sqrt{1+c^2}}(\Psi_9+c\Psi_{10})$	$-\frac{3}{2}Z^2+\left(\frac{19148633}{5598720}-\frac{1}{3359232}\sqrt{221876564389}\right)Z$	$\frac{1}{98415}(\sqrt{221876564389}-460642)$	-34.3202	0.1056
	$^5S^\circ$	Ψ_4	$-\frac{3}{2}Z^2+\frac{464555}{139968}Z$		-34.0859	
	^1S	$\frac{1}{\sqrt{1+c^2}}(\Psi_1+c\Psi_2)$	$-\frac{3}{2}Z^2+\left(\frac{966289}{279936}-\frac{1}{1679616}\sqrt{62733275266}\right)Z$	$-\frac{1}{98415}(\sqrt{62733275266}-230321)$	-34.1838	-0.2047
	$^3D^\circ$	Ψ_{12}	$-\frac{3}{2}Z^2+\frac{4730843}{1399680}Z$		-33.7203	
	$^3P^\circ$	Ψ_8	$-\frac{3}{2}Z^2+\frac{1904147}{559872}Z$		-33.5938	
	$^1D^\circ$	Ψ_{11}	$-\frac{3}{2}Z^2+\frac{9625711}{2799360}Z$		-33.3688	
	$^3S^\circ$	Ψ_3	$-\frac{3}{2}Z^2+\frac{961915}{279936}Z$		-33.3828	
	$^1P^\circ$	Ψ_5	$-\frac{3}{2}Z^2+\frac{242119}{69984}Z$		-33.2422	
	^3P	$\frac{1}{\sqrt{1+c^2}}(\Psi_6+c\Psi_7)$	$-\frac{3}{2}Z^2+\left(\frac{3806107}{1119744}+\frac{1}{3359232}\sqrt{221876564389}\right)Z$	$\frac{1}{98415}(\sqrt{221876564389}+460642)$	-32.7641	9.4668
	^1D	$\frac{1}{\sqrt{1+c^2}}(\Psi_9+c\Psi_{10})$	$-\frac{3}{2}Z^2+\left(\frac{19148633}{5598720}+\frac{1}{3359232}\sqrt{221876564389}\right)Z$	$\frac{1}{98415}(-\sqrt{221876564389}-460642)$	-32.6376	-9.4668
	^1S	$\frac{1}{\sqrt{1+c^2}}(\Psi_1+c\Psi_2)$	$-\frac{3}{2}Z^2+\left(\frac{966289}{279936}+\frac{1}{1679616}\sqrt{62733275266}\right)Z$	$\frac{1}{98415}(\sqrt{62733275266}+230321)$	-32.3943	4.8853

Asymptotic Schrödinger energy levels, Li–C

	Symm.	Ψ	E	c	E (num.)	c (num.)
N	${}^4S^\circ$	Ψ_2	$-\frac{13}{8}Z^2 + \frac{2437421}{559872}Z$		-49.1503	
	${}^2D^\circ$	Ψ_7	$-\frac{13}{8}Z^2 + \frac{24551357}{5598720}Z$		-48.9288	
	${}^2P^\circ$	$\frac{1}{\sqrt{1+c^2}}(\Psi_3 + c\Psi_4)$	$-\frac{13}{8}Z^2 + \frac{1}{6718464}(30636167 - \sqrt{1144203315841})Z$	$-\frac{1}{393660}(\sqrt{1144203315841} - 1032821)\sqrt{2}$	-48.8195	-0.1324
	${}^4P$	Ψ_6	$-\frac{13}{8}Z^2 + \frac{7549145}{1679616}Z$		-48.1630	
	${}^2D$	Ψ_8	$-\frac{13}{8}Z^2 + \frac{76337819}{16796160}Z$		-47.8103	
	${}^2S$	Ψ_1	$-\frac{13}{8}Z^2 + \frac{3843463}{839808}Z$		-47.5888	
	${}^2P$	Ψ_5	$-\frac{13}{8}Z^2 + \frac{15393535}{3359232}Z$		-47.5478	
	${}^2P^\circ$	$\frac{1}{\sqrt{1+c^2}}(\Psi_3 + c\Psi_4)$	$-\frac{13}{8}Z^2 + \frac{1}{6718464}(30636167 + \sqrt{1144203315841})Z$	$\frac{1}{393660}(\sqrt{1144203315841} + 1032821)\sqrt{2}$	-46.5905	7.5532
O	${}^3P$	Ψ_5	$-\frac{7}{4}Z^2 + \frac{4754911}{839808}Z$		-66.7048	
	${}^1D$	Ψ_6	$-\frac{7}{4}Z^2 + \frac{47726257}{8398080}Z$		-66.5360	
	${}^1S$	$\frac{1}{\sqrt{1+c^2}}(\Psi_1 + c\Psi_2)$	$-\frac{7}{4}Z^2 + \frac{1}{1679616}(9884485 - \sqrt{89111336179})Z$	$-\frac{1}{295245}(2\sqrt{89111336179} - 572179)\sqrt{3}$	-66.3421	-0.1458
	${}^3P^\circ$	Ψ_4	$-\frac{7}{4}Z^2 + \frac{1224899}{209952}Z$		-65.3265	
	${}^1P^\circ$	Ψ_3	$-\frac{7}{4}Z^2 + \frac{9897607}{1679616}Z$		-64.8578	
	${}^1S$	$\frac{1}{\sqrt{1+c^2}}(\Psi_1 + c\Psi_2)$	$-\frac{7}{4}Z^2 + \frac{1}{1679616}(9884485 + \sqrt{89111336179})Z$	$\frac{1}{295245}(2\sqrt{89111336179} + 572179)\sqrt{3}$	-63.4984	6.8592
F	${}^2P^\circ$	Ψ_2	$-\frac{15}{8}Z^2 + \frac{11982943}{1679616}Z$		-87.6660	
	${}^2S$	Ψ_1	$-\frac{15}{8}Z^2 + \frac{4108267}{559872}Z$		-85.8342	
Ne	${}^1S$	Ψ_1	$-2Z^2 + \frac{2455271}{279936}Z$		-112.2917	

Asymptotic Schrödinger energy levels, N–Ne

Some proof ingredients

- Scaling: $\tilde{\Psi}(x) = Z^{3N/2}\Psi(Zx)$, $\tilde{E} = Z^{-2}E$
  Preserves L^2 norm
  Equation becomes $(-\frac{1}{2}\Delta - \sum_{j=1}^{N}\frac{1}{|x_j|} + \frac{1}{Z}\sum_{i<j}\frac{1}{|x_i - x_j|})\tilde{\Psi} = \tilde{E}\tilde{\Psi}$
- Perturbation theory: For large Z, all the action is in a finite dim subspace. More precisely: asymptotics governed by $PHP\Psi = E\Psi$, P=projector onto non-interacting GS. ("PT model")
- Hydrogen atom theory + theory of non-interacting fermions: Can determine non-interacting GS explicitly. Dimension for He, Li, Be, B, C, N, O, F, Ne: 1, 8, 28, 56, 70, 56, 28, 8, 1

Some proof ingredients, ctd

Difficulties:

- Non-interacting GS (i.e. state space of PT model) of somewhat daunting looking dimension
- PT Hamiltonian PHP easy to write down abstractly, but need method to determine it explicitly
- PT model is a strongly interacting many-body model.

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- PT model is a strongly interacting many-body model.

Overcome these by

- decomposition of PHP into small invariant blocks via
  – careful use of symmetry group and its repr.theory
  – Introduction of a Hodge operator (El.-hole duality)
- explicit determination of PHP via
  – identities from quantum chemistry ('Slater's rules')
  – Fourier calculus (e.g. need FT of products of hydr.orbitals)
  – Residue calculus (evaluation of 1D rational integrals)

Math. picture of periodic table, 1: L and S values

Key point: These are closely related to the notion of ‘group’ in the periodic table

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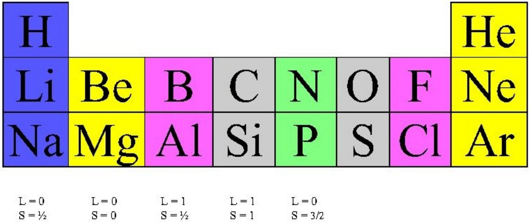

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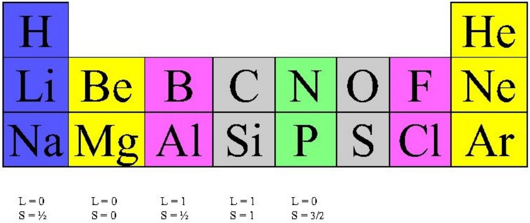

- Gradients of (L, S) with respect to atomic number would separate the group 3 metals from the halogens, and the Carbon group from the oxygen group

L and S values and crystal lattice structures

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Unlike the first three elements (H, He, Li), which are fcc, liquid, fcc at low temperature, it has a very complicated ground state.

It is clear from the lack of radial symmetry that even a minimal model would have to account for the internal rotational degrees of freedom; a potential depending only on the positional degrees of freedom is no good.

Math. picture of periodic table, 2: Electronic structure

Our asymptotic ground states provide for the first time a mathematical explanation of the semi-empirical "hydrogen orbital configurations" developed by Bohr, Hund and Slater to explain the periodic table.

These configurations are based on 3 semi-empirical postulates:

(a) Each electron in an atom occupies a hydrogenic orbital.

(b) *Sub-shell ordering* The orbitals in each hydrogen energy level, or shell, form sub-shells which are occupied in the order
$1s \quad 2s \quad 2p \quad 3s \quad 3p \quad 4s \quad 3d \quad \ldots$

(c) *Hund's rule* Within any partially filled sub-shell, the electrons adopt a configuration with the greatest possible number of aligned spins.

Example In Carbon the six electrons would occupy the orbitals
$1s\!\uparrow 1s\!\downarrow 2s\!\uparrow 2s\!\downarrow 2p_1\!\uparrow 2p_2\!\uparrow$.

Alternative choices $2p_1\!\downarrow$ or $2p_2\!\downarrow$ for the last orbital obey (b) but not (c)

Math. picture of periodic table, 2: Electronic structure

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Corrections to semi-empirical rules:

- Alongside any Slater determinant, the asymptotic GS contains its orbit under the many-electron symmetry group
- sub-shell ordering not strictly obeyed: for Be, B, C, 10 to 20 percent corrections from "higher" sub-shells also present
- In rare cases (such as the lowest ${}^1D$ and ${}^5S$ states of Carbon) ordering of excited states disagrees with Hund's rules (with experiment confirming our ordering).

Math. picture of the periodic table, 3: Excited levels

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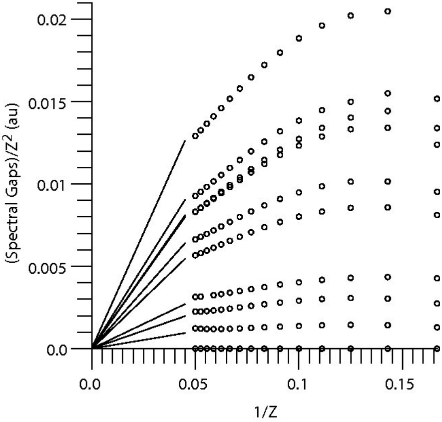

Lines: Asymptotic Schrödinger levels [GF/Goddard]
Circles: experiment [NIST atomic spectra database].
Use of scaled axes suggested by our analysis, and to our knowledge new.

For the highest level at $Z = 6$ and the fourth level at $Z = 18$, we were unable to find experimental data.

Math. picture of the periodic table, 4: ionization energies

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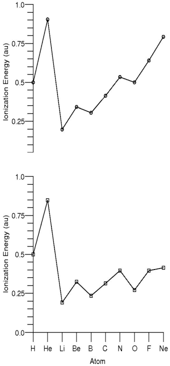
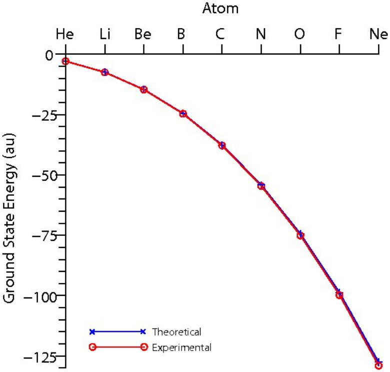
Asymptotics-based low-dimensional numerical method: captures, at least qualitatively, the bizarre experimental graph



More about asymptotics-based low-dimensional numerics

Total energies extremely well captured; our about 50 DOF's competitive with large-scale studies with about 10^8 DOF's



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The semi-empirical hydrogen orbital configurations of Bohr, Hund and Slater have a precise mathematical meaning, as asymptotic limits of true Schrödinger ground states for large nuclear charge.

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This provides a theoretical alternative to semi-empirical discussions of the periodic table in the literature, and a rare benchmark for the design and validation of computational methods.

Lessons from John Ball

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MSc course notes, An introduction to variational methods for PDE's, 16 January, 1991

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"[This course] takes certain philosophical positions.

First, *the problem is the key*; it is no use spending a lot of time and energy learning new methods if in the end you apply them to a poor problem. This has the corollary that *mathematicians should take responsibility for the models they analyse*. They should know where they come from, how to derive them, what the starting assumptions are, and why they are of interest to science. It is not sufficient to accept the word of a physicist, biologist, or another mathematician, or the author, that such and such a model or problem is a good one. This is not just an insurance policy, since the underlying science of a model is often crucial for its analysis..."

Lessons from John Ball, ctd

"Second, that *the analysis of the problem be rigorous* (that is, right and proved to be so). Whatever approximations we made in deriving the model, we make no approximations in its analysis except those justified by theorems. Thus, any results obtained are a true test of the model. This is an aim, not a fetish. The problems posed by the PDE's of pure and applied science can be of immense difficulty and beyond the reach of known rigorous techniques. In this case, it is common sense to use approximation methods and numerical studies (which are crucial tools for discovering new phenomena), or to consider simplified equations, isolating some key difficulty of the original problem. But we should distinguish carefully between conjectures based on these methods and proved theorems."

Lessons from John Ball, ctd

"Third, that *no artificial distinction be drawn between pure and applied mathematics*. If you like, this is a combination of the two preceding positions. We maximize the chances of success by moving as freely as possible between the science of the model and any branch of mathematics appropriate for its analysis. ... The unity of the modelling/analysis process was second nature to many of the greatest mathematicians of previous generations, such as Newton, Euler, Riemann, and Cauchy. For example, Cauchy made fundamental advances both in developing continuum models of solids and fluids and in inventing numerous techniques for their analysis, including complex integration theory and many basic tools of real analysis..."

Happy birthday John!