

Asymptotic limits of the Schrödinger equation and computational method development in electronic structure theory

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So, a good computational method should predict this.

HF and DFT do, for small atoms. This is remarkable.

But what happens for slightly larger atoms is equally remarkable.

Orbital filling, 3d transition metal series, various methods

Atom	Madelung	HF	Rel.HF	LSDA	Becke 88	B3LYP	Expt.
Sc	$4s^2 3d^1$	$4s^2 3d^1$	$4s^2 3d^1$	$4s^2 3d^1$	$4s^2 3d^1$	$4s^2 3d^1$	$4s^2 3d^1$
Ti	$4s^2 3d^2$	$4s^2 3d^2$	$4s^2 3d^2$	$4s^2 3d^2$	$4s^1 3d^3$	$4s^2 3d^2$	$4s^2 3d^2$
V	$4s^2 3d^3$	$4s^2 3d^3$	$4s^2 3d^3$	$4s^1 3d^4$	$4s^1 3d^4$	$4s^1 3d^4$	$4s^2 3d^3$
Cr	$4s^2 3d^4$	$4s^2 3d^4$	$4s^1 3d^5$	$4s^1 3d^5$	$4s^1 3d^5$	$4s^1 3d^5$	$4s^1 3d^5$
Mn	$4s^2 3d^5$	$4s^2 3d^5$	$4s^1 3d^6$	$4s^2 3d^5$	$4s^2 3d^5$	$4s^2 3d^5$	$4s^2 3d^5$
Fe	$4s^2 3d^6$	$4s^2 3d^6$	$4s^1 3d^7$	$4s^2 3d^6$	$4s^2 3d^6$	$4s^2 3d^6$	$4s^2 3d^6$
Co	$4s^2 3d^7$	$4s^2 3d^7$	$4s^2 3d^7$	$4s^1 3d^8$	$4s^2 3d^7$	$4s^1 3d^8$	$4s^2 3d^7$
Ni	$4s^2 3d^8$	$4s^2 3d^8$	$4s^1 3d^9$	$4s^1 3d^9$	$4s^1 3d^9$	$4s^1 3d^9$	$4s^2 3d^8$
Cu	$4s^2 3d^9$	$4s^2 3d^9$	$4s^1 3d^{10}$	$4s^1 3d^{10}$	$4s^1 3d^{10}$	$4s^1 3d^{10}$	$4s^1 3d^{10}$

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Ti	$4s^2 3d^2$	$4s^2 3d^2$	$4s^2 3d^2$	$4s^2 3d^2$	$4s^1 3d^3$	$4s^2 3d^2$	$4s^2 3d^2$
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Madelung rule: Fill in order of increasing $n + \ell$ (\sim no. of nodes of the wavefunction)

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Experiment: Classification of Ni as $4s^2$ should be viewed with caution.

Summary (3d transition metal series)

- All methods get at least 2 out of 9 elements wrong.
- 8 out of 9 elements come out wrong in some method.

Goal

Revisit transition metal atoms from a careful wavefunction point of view.

NOT large N method (e.g. a DFT that fixes this) → *too ambitious*

Instead, want **accuracy** (reference for approximate calculations) and **better understanding** (identify essential DOF's of the WF).

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Ch.Mendl, GF, to appear in J.Chem.Phys., arXiv:1009.2013

Efficient algorithm; appl. to transition metal atoms

Exact ground states in fixed-N-large-Z limit

Starting point: full (non-relativistic, Born-Oppenheimer)
Schrödinger eq.

- ▶ N electrons, one nucleus of charge Z (neutral atoms: $N=Z$)
- ▶ Electronic structure described by $\Psi : (\mathbb{R}^3 \times \mathbb{Z}_2)^N \rightarrow \mathbb{C}$
- ▶ Governing eq.: $H\Psi = E\Psi$, nonrel. Ham.: $H = -\frac{1}{2}\Delta + V(x)$
- ▶ Potential: Coulomb el-nuc attraction, el-el repulsion

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

- ▶ Antisymmetry: $\Psi(\dots, x_i, s_i, \dots, x_j, s_j, \dots) = -\Psi(\dots, x_j, s_j, \dots, x_i, s_i, \dots)$

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Now take limit $Z \rightarrow \infty$ with N fixed

Corresponds physically to iso-electronic sequence like Li, Be^+ , B^{2+} , C^{3+} , ...

e.g. Hylleraas 1930, Layzer 1959, Wilson 1984, Beyer et al. 1997, Currell 2003

Exact ground states in fixed-N-large-Z limit, ctd

Theorem

For $N = 1, \dots, 10$, and in the limit $Z \rightarrow \infty$, the difference between the true solutions to the Schrödinger equation and the simple wave functions given in the table on the next slide tends to zero (in a least squares sense).

GF, Goddard, Phys.Rev.A 81, 032516, 2010; SIAM J.Math.Anal. 41, 631, 2009

Iso-el. sequence	Symmetry	Ground state	Dimension
H	2S	$ 1s\rangle, 1s\rangle$	2
He	1S	$ 1s^2\rangle$	1
Li	2S	$ 1s^22s\rangle, 1s^2\bar{2}s\rangle$	2
Be	1S	$\frac{1}{\sqrt{1+c^2}} \left(1s^22s^2\rangle + c \frac{1}{\sqrt{3}} \left(1s^22p_1^2\rangle + 1s^22p_2^2\rangle + 1s^22p_3^2\rangle \right) \right)$ $c = -\frac{\sqrt{3}}{50049} (2\sqrt{1509308377} - 69821) = -0.2310995\dots$	1
B	$^2P^o$	$\frac{1}{\sqrt{1+c^2}} \left(1s^22s^22p_i\rangle + c \frac{1}{\sqrt{2}} \left(1s^22p_i2p_j^2\rangle + 1s^22p_i2p_k^2\rangle \right) \right)$ $\frac{1}{\sqrt{1+c^2}} \left(1s^22s^2\bar{2}p_i\rangle + c \frac{1}{\sqrt{2}} \left(1s^2\bar{2}p_i2p_j^2\rangle + 1s^2\bar{2}p_i2p_k^2\rangle \right) \right)$ $(i, j, k) = (3, 1, 2), (1, 2, 3), (2, 3, 1)$ $c = -\frac{\sqrt{2}}{393660} (\sqrt{733174301809} - 809747) = -0.1670823\dots$	6
C	3P	$\frac{1}{\sqrt{1+c^2}} \left(1s^22s^22p_i2p_j\rangle + c 1s^22p_k^22p_i2p_j\rangle \right)$ $\frac{1}{\sqrt{1+c^2}} \left(\frac{1}{\sqrt{2}} \left(1s^22s^22p_i2p_j\rangle + 1s^22s^2\bar{2}p_i2p_j\rangle \right) + c \frac{1}{\sqrt{2}} \left(1s^22p_k^22p_i2p_j\rangle + 1s^22p_k^2\bar{2}p_i2p_j\rangle \right) \right)$ $\frac{1}{\sqrt{1+c^2}} \left(1s^22s^2\bar{2}p_i2p_j\rangle + c 1s^22p_k^2\bar{2}p_i2p_j\rangle \right)$ $(i, j, k) = (3, 1, 2), (1, 2, 3), (2, 3, 1)$ $c = -\frac{1}{98415} (\sqrt{221876564389} - 460642) = -0.1056317\dots$	9
N	$^4S^o$	$ 1s^22s^22p_12p_22p_3\rangle$ $\frac{1}{\sqrt{3}} \left(1s^22s^2\bar{2}p_32p_12p_2\rangle + 1s^22s^22p_3\bar{2}p_12p_2\rangle + 1s^22s^22p_32p_1\bar{2}p_2\rangle \right)$ $\frac{1}{\sqrt{3}} \left(1s^22s^2\bar{2}p_3\bar{2}p_12p_2\rangle + 1s^22s^2\bar{2}p_32p_1\bar{2}p_2\rangle + 1s^22s^23\bar{2}p_1\bar{2}p_2\rangle \right)$	4
O	3P	$ 1s^22s^2\bar{2}p_12p_22p_3\rangle$ $ 1s^22s^22p_i^22p_j2p_k\rangle$ $\frac{1}{\sqrt{2}} \left(1s^22s^22p_i^22p_j2p_k\rangle + 1s^22s^22p_j^22p_i2p_k\rangle \right)$ $ 1s^22s^22p_i^2\bar{2}p_j2p_k\rangle$ $(i, j, k) = (3, 1, 2), (1, 2, 3), (2, 3, 1)$	9
F	$^2P^o$	$ 1s^22s^22p_i^22p_j^22p_k\rangle$ $ 1s^22s^22p_i^22p_j^2\bar{2}p_k\rangle$ $(i, j, k) = (3, 1, 2), (1, 2, 3), (2, 3, 1)$	6
Ne	1S	$ 1s^22s^22p_1^22p_2^22p_3^2\rangle$	1

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

Notation

Hypergeometric functions (diluted hydrogen eigenstates)

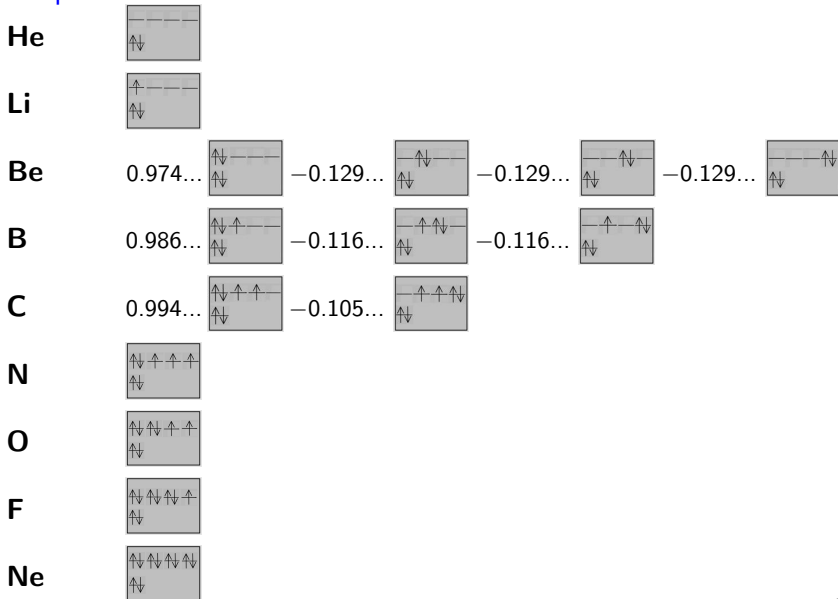
$$1s(x) = \frac{Z^{3/2}}{\sqrt{\pi}} e^{-Z|x|}, \quad \phi_{1s} : \mathbb{R}^3 \rightarrow \mathbb{C} \text{ (1s-orbital)}$$

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

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

Iso-el.
Seq.

Schrödinger ground state in the limit $Z \rightarrow \infty$



Also, have determined the first few higher energy levels and eigenspaces in closed form. A bit too complicated to record here.

	Symm.	Ψ	E	c	E (num.)	c (num.)
Li	$2S$	Ψ_1	$-\frac{1}{2}Z^2 + \frac{5965}{2428}Z$		-7.0566	
	$2P^o$	Ψ_2	$-\frac{1}{2}Z^2 + \frac{47307}{2428}Z$		-6.8444	
Be	$1S$	$\frac{1}{\sqrt{1+c^2}}(\Psi_1 + c\Psi_2)$	$-\frac{1}{2}Z^2 + \frac{1679616}{1799616}(2813231 - 5\sqrt{1509308377})Z$	$-\frac{1}{59049}(2\sqrt{1509308377} - 6981)\sqrt{3}$	-13.7629	-0.2311
	$3P^o$	Ψ_4	$-\frac{1}{2}Z^2 + \frac{1363965}{839808}Z$		-13.5034	
	$1D^o$	Ψ_3	$-\frac{1}{2}Z^2 + \frac{4826353}{1419600}Z$		-13.2690	
	$3P$	Ψ_5	$-\frac{1}{2}Z^2 + \frac{1339694}{1419600}Z$		-13.0955	
	$1D$	Ψ_6	$-\frac{1}{2}Z^2 + \frac{14673197}{8398080}Z$		-13.0112	
	$1S$	$\frac{1}{\sqrt{1+c^2}}(\Psi_1 + c\Psi_2)$	$-\frac{1}{2}Z^2 + \frac{1679616}{1799616}(2813231 + 5\sqrt{1509308377})Z$	$\frac{1}{59049}(2\sqrt{1509308377} + 6981)\sqrt{3}$	-12.8377	4.3271
B	$2D^o$	$\frac{1}{\sqrt{1+c^2}}(\Psi_3 + c\Psi_4)$	$-\frac{11}{8}Z^2 + \frac{6718464}{2006759}(16493659 - \sqrt{733174301809})Z$	$-\frac{1}{393660}(\sqrt{733174301809} - 809747)\sqrt{2}$	-22.7374	-0.1671
	$4P$	Ψ_6	$-\frac{11}{8}Z^2 + \frac{2006759}{839808}Z$		-22.4273	
	$2D$	Ψ_7	$-\frac{11}{8}Z^2 + \frac{60981549}{16795160}Z$		-22.1753	
	$2S$	Ψ_1	$-\frac{11}{8}Z^2 + \frac{4131259}{16795160}Z$		-22.0171	
	$2P$	Ψ_5	$-\frac{11}{8}Z^2 + \frac{1639416}{3359232}Z$		-21.9878	
	$4S^o$	Ψ_2	$-\frac{11}{8}Z^2 + \frac{706213}{14307407}Z$		-21.7612	
	$2D^o$	Ψ_8	$-\frac{11}{8}Z^2 + \frac{14307407}{5598720}Z$		-21.6030	
	$2P^o$	$\frac{1}{\sqrt{1+c^2}}(\Psi_3 + c\Psi_4)$	$-\frac{11}{8}Z^2 + \frac{6718464}{2006759}(16493659 + \sqrt{733174301809})Z$	$\frac{1}{393660}(\sqrt{733174301809} + 809747)\sqrt{2}$	-21.4629	5.9851
C	$3P$	$\frac{1}{\sqrt{1+c^2}}(\Psi_6 + c\Psi_7)$	$-\frac{3}{2}Z^2 + \frac{3863107}{1119744} - \frac{1}{3359232}\sqrt{221876564389}Z$	$-\frac{1}{98415}(\sqrt{221876564389} - 460642)$	-34.4468	-0.1056
	$1D$	$\frac{1}{\sqrt{1+c^2}}(\Psi_9 + c\Psi_{10})$	$-\frac{3}{2}Z^2 + \frac{19148633}{5598720} - \frac{1}{3359232}\sqrt{221876564389}Z$	$\frac{1}{98415}(\sqrt{221876564389} - 460642)$	-34.3202	0.1056
	$5S^o$	Ψ_4	$-\frac{3}{2}Z^2 + \frac{464555}{339965}Z$		-34.0859	
	$1S$	$\frac{1}{\sqrt{1+c^2}}(\Psi_1 + c\Psi_2)$	$-\frac{3}{2}Z^2 + \frac{996289}{779360} - \frac{1}{1679616}\sqrt{62733275266}Z$	$-\frac{1}{98415}(\sqrt{62733275266} - 230321)$	-34.1838	-0.2047
	$3D^o$	Ψ_{12}	$-\frac{3}{2}Z^2 + \frac{2730843}{339965}Z$		-33.7203	
	$3P^o$	Ψ_8	$-\frac{3}{2}Z^2 + \frac{1464342}{339965}Z$		-33.5938	
	$1D^o$	Ψ_{11}	$-\frac{3}{2}Z^2 + \frac{559874}{679320}Z$		-33.3688	
	$3S^o$	Ψ_3	$-\frac{3}{2}Z^2 + \frac{679320}{279932}Z$		-33.3828	
	$1P^o$	Ψ_5	$-\frac{3}{2}Z^2 + \frac{242110}{59964}Z$		-33.2422	
	$3P$	$\frac{1}{\sqrt{1+c^2}}(\Psi_6 + c\Psi_7)$	$-\frac{3}{2}Z^2 + \frac{3863107}{1119744} + \frac{1}{3359232}\sqrt{221876564389}Z$	$\frac{1}{98415}(\sqrt{221876564389} + 460642)$	-32.7641	9.4668
	$1D$	$\frac{1}{\sqrt{1+c^2}}(\Psi_9 + c\Psi_{10})$	$-\frac{3}{2}Z^2 + \frac{19148633}{5598720} + \frac{1}{3359232}\sqrt{221876564389}Z$	$\frac{1}{98415}(-\sqrt{221876564389} - 460642)$	-32.6376	-9.4668
	$1S$	$\frac{1}{\sqrt{1+c^2}}(\Psi_1 + c\Psi_2)$	$-\frac{3}{2}Z^2 + \frac{996289}{279932} + \frac{1}{1679616}\sqrt{62733275266}Z$	$\frac{1}{98415}(\sqrt{62733275266} + 230321)$	-32.3943	4.8853

Asymptotic Schrödinger energy levels, Li-C

	Symm.	Ψ	E	c	E (num.)	c (num.)
N	$4S^o$	Ψ_2	$-\frac{13}{8}Z^2 + \frac{4514241}{599579}Z$		-49.1503	
	$2D^o$	Ψ_7	$-\frac{13}{8}Z^2 + \frac{44531357}{5998720}Z$		-48.9288	
	$2P^o$	$\frac{1}{\sqrt{1+c}}(\Psi_3 + c\Psi_4)$	$-\frac{13}{8}Z^2 + \frac{1}{8719484}(30636167 - \sqrt{1144203315841})Z$	$-\frac{1}{393660}(\sqrt{1144203315841} - 1032821)\sqrt{2}$	-48.8195	-0.1324
	$4P$	Ψ_6	$-\frac{13}{8}Z^2 + \frac{7549145}{1679616}Z$		-48.1630	
	$2D$	Ψ_8	$-\frac{13}{8}Z^2 + \frac{76337819}{16795168}Z$		-47.8103	
	$2S$	Ψ_1	$-\frac{13}{8}Z^2 + \frac{3811463}{839808}Z$		-47.5888	
	$2P$	Ψ_5	$-\frac{13}{8}Z^2 + \frac{13393539}{1347232}Z$		-47.5478	
	$2P^o$	$\frac{1}{\sqrt{1+c}}(\Psi_3 + c\Psi_4)$	$-\frac{13}{8}Z^2 + \frac{1}{8719484}(30636167 + \sqrt{1144203315841})Z$	$\frac{1}{393660}(\sqrt{1144203315841} + 1032821)\sqrt{2}$	-46.5905	7.5532
O	$3P$	Ψ_5	$-\frac{7}{2}Z^2 + \frac{4754911}{839808}Z$		-66.7048	
	$1D$	Ψ_6	$-\frac{7}{2}Z^2 + \frac{4774637}{8398080}Z$		-66.5360	
	$1S$	$\frac{1}{\sqrt{1+c}}(\Psi_1 + c\Psi_2)$	$-\frac{7}{2}Z^2 + \frac{1679616}{1679616}(9884485 - \sqrt{89111336179})Z$	$-\frac{1}{295245}(2\sqrt{89111336179} - 572179)\sqrt{3}$	-66.3421	-0.1458
	$3P^o$	Ψ_4	$-\frac{7}{2}Z^2 + \frac{1224899}{1679616}Z$		-65.3265	
	$1P^o$	Ψ_3	$-\frac{7}{2}Z^2 + \frac{697607}{1679616}Z$		-64.8578	
	$1S$	$\frac{1}{\sqrt{1+c}}(\Psi_1 + c\Psi_2)$	$-\frac{7}{2}Z^2 + \frac{1679616}{1679616}(9884485 + \sqrt{89111336179})Z$	$\frac{1}{295245}(2\sqrt{89111336179} + 572179)\sqrt{3}$	-63.4984	6.8592
F	$2P^o$	Ψ_2	$-\frac{15}{8}Z^2 + \frac{11982943}{1679616}Z$		-87.6660	
	$2S$	Ψ_1	$-\frac{15}{8}Z^2 + \frac{4108267}{1679616}Z$		-85.8342	
Ne	$1S$	Ψ_1	$-2Z^2 + \frac{4356211}{279936}Z$		-112.2917	

Asymptotic Schrödinger energy levels, N-Ne

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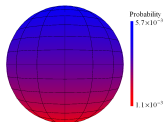
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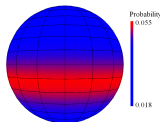
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- ▶ For 7 out of 10 elements, the limiting eigenspace contains a Slater determinant, i.e. the HF energy would become exact
- ▶ For the remaining 3 elements, Be, B and C, 10 to 20 percent correction by a very particular “higher subshell” configuration ($2s^2$ electron pair migrates to a $2p$ orbital, while remaining paired with opposite spin)
- ▶ Challenge for DFT theorists: find a functional that gets this right. (Note: we have an exact formula for the whole $\rho(x)$.)

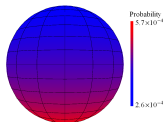
Physical significance of the corrections



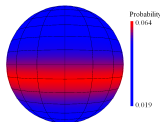
high charge ion, Be sequence (exact)



high charge ion, N sequence (exact)



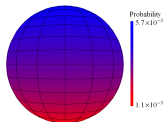
neutral Be (numerical)



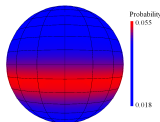
neutral N (numerical)

Quantum probability of finding a second electron anywhere on the sphere of radius N/Z a.u. when the first electron is at the north pole, for the ground state. Mathematically: Pair density $\rho_2(x_0, y)$, x_0 =north pole

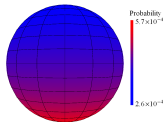
Physical significance of the corrections



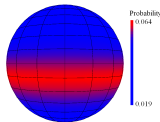
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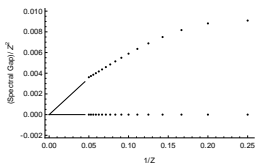
For Be, **neglecting the corrections** to the standard $1s^2 2s^2$ config. would lead to the **unphysical result of a constant probability**.

Large- Z excited levels vs. experiment

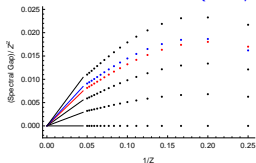
When comparing to experiment, don't plot bare levels E as function of nuclear charge Z , but renormalize so as to make E and Z constant at $Z = \infty$.

Achieved by plotting $\frac{E}{Z^2}$ as a function of $\frac{1}{Z}$.

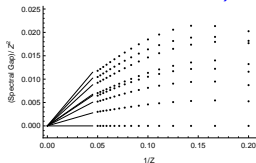
Large- Z excited levels vs. experiment (GF/Goddard, PRA 2010)



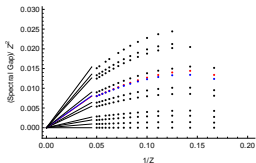
Lithium, $N = 3$



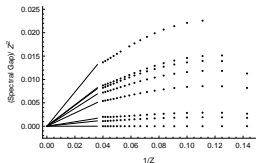
Beryllium, $N = 4$



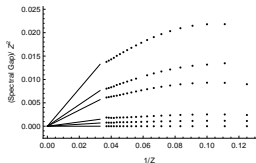
Boron, $N = 5$



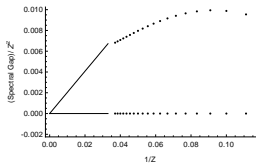
Carbon, $N = 6$



Nitrogen, $N = 7$



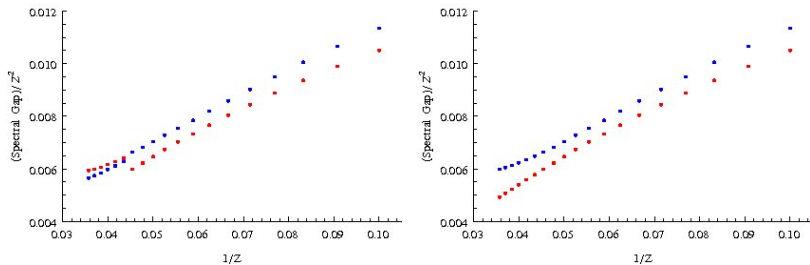
Oxygen, $N = 8$



Fluorine, $N = 9$

Dots: Experimental levels [NIST]; Lines: Tangents to exact Schröd. levels at $\frac{1}{Z} = 0$ [Friescke/Goddard]

Correction of experimental L and S assignments



Experimental energies of five-electron ions as assigned by NIST, averaged over J (left) and with the the 2S and 2P $J = 1/2$ levels transposed for $Z \geq 19$ before averaging (right).

The fact that the theoretical levels should lie on smooth curves *strongly suggests* that the assignment by NIST is incorrect.

Asymptotics-based CI

GF, Goddard, Multiscale Meth. Simul., 2009

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Main idea: resolve gaps and wavefunctions correctly in large- Z limit, at fixed finite model dimension.

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- ▶ Resulting method works well in practice when $Z = N$

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Asymptotics-based CI: Theoretical selection criteria

1. Preservation of symmetries
2. Virial theorem
3. Asymptotic exactness of low-lying e-states and gaps in the limit $Z \rightarrow \infty$, at fixed finite subspace dimension.

Asymptotics-based CI

- (A) (Choice of a parametrized, asymptotically exact family of subspaces)
 $V_{n\ell}(\mathbf{Z}) = \text{Span of Slater orbitals with radial/angular quantum numbers } n \text{ and } \ell$
 $\mathbf{Z} = (Z_{n\ell})$: vector of orbital exponents (dilation parameters)
 $\mathbf{d} = (d_{n\ell})$: vector of occupation numbers of the $V_{n\ell}$
 $V_{\mathbf{d}}(\mathbf{Z}) = \text{"Configuration"} = \text{Span of all Slater determinants with } d_{n\ell} \text{ orbitals from } V_{n\ell}$
Constraints on \mathbf{d} :
 $\sum d_{n\ell} = N$ and, e.g.,
 $d_{n\ell} = 2 \cdot (2\ell + 1)$ for $(n, \ell) \leq (n, \ell)_{min}$ (core shells fully occupied)
 $d_{n\ell} = 0$ for $(n, \ell) > (n, \ell)_{max}$ (shells above a cutoff empty)
 $V(\mathbf{Z}) = \text{Span of union of all "configurations" } V_{\mathbf{d}}(\mathbf{Z}) \text{ with } \mathbf{d} \text{ satisfying above constraints}$
- (B) (Symmetry decomposition)
Decompose V into irreducible subspaces V_{sym} of the symmetry group $SU(2) \times SO(3) \times \mathbb{Z}_2$
(i.e., compute simultaneous eigenspaces of the many-body angular momentum, spin, and parity operators $\underline{L}^2, \underline{L}_3, \underline{S}^2, \underline{S}_3$, parity)
- (C) (Subspace eigenvalue problem)
 $E^{CI}(\mathbf{Z}) :=$ (lowest or higher) eigenvalue of $P(\mathbf{Z})HP(\mathbf{Z})$ on $V_{sym}(\mathbf{Z})$,
 $\Psi^{CI}(\mathbf{Z}) :=$ corresponding normalized eigenstate,
where $P(\mathbf{Z}) =$ orthogonal projector of $L_a^2((\mathbb{R}^3 \times \mathbb{Z}_2)^N)$ onto $V_{sym}(\mathbf{Z})$
- (D) (Variational parameter determination)
 $Z_* := \text{argmin}_{\mathbf{Z}} E^{CI}(\mathbf{Z})$, $E^{CI} := E^{CI}(Z_*)$, $\Psi^{CI} := \Psi^{CI}(Z_*)$

Not really a new method – rather an **interesting specific choice** within a well known range of models, arrived at by asymptotics (instead of “construction” / “empiricism”)

Theoretical properties of asymptotics-based CI

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- ▶ **Symmetry preservation**: the CI subspace V is invariant under the many-body spin, angular momentum, and parity operators. Hence well defined many-body quantum numbers L , S , and p
- ▶ **Virial theorem** (because orbital exponents are determined self-consistently for the actual CI wavefunctions, instead of precomputing them via a HF calculation)

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Essential features without which asymptotic exactness would fail:

- Slater type orbitals (STO's) instead of Gaussians
- Inclusion of *all*, not just *some* configurations satisfying the occ.constraints.

Numerical results

F./Goddard, Mult.Model.Simul.2009

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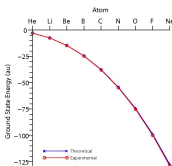
Even *minimal* as.-based CI (all core orbitals occupied, all higher-than-valence orbitals unoccupied) does remarkably well:

Total energies for He to Ne within 1 percent of experiment

Fully competitive with MDHF at much fewer DOF's

e.g.: for lowest 10 or so levels for He to Ne, **nearly all orderings right** (except switch 2 nbring higher levels in Be and C, both of which are wrong in MDHF also)

Our 10 to 50 DOF's never beaten by more then a factor 8 or so by *any* method, including large-scale studies with about 10^8 DOF's



Numerical results for transition metal atoms

Ch.Mendl, GF, to appear in J.Chem.Phys., 2010

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(First experimental contradiction to the empirical Pauli/Madelung $4s < 3d$ rule: Chromium, which has $N=24$ electrons, is supposed to have 18 [Argon] closed-shell electrons, 2 2s electrons, and 4 3d electrons. But its experimental L and S values suggest only 1 2s electron, but 5 3d electrons! Particularly subtle because its predecessors Ca, Sc, Ti, V all come out with 2 2s electrons.)

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	sym	conf.	dim	E_{ABCI}	Z_{1s}	Z_{2s}	Z_{2p}	Z_{3s}	Z_{3p}	Z_{3d}	Z_{4s}	Z_{4p}	Z_{4d}
Ca	3D	$4s^1$	2	-674.1634	19.68	17.41	16.13	12.05	10.38	2.83	5.43	-	2.46
	1S	$4s^2$	1	-674.2442	19.68	17.41	16.13	12.10	10.38	-	5.03	-	-
Sc	4F	$4s^1$	3	-756.9381	20.68	18.42	17.15	12.99	11.30	8.26	5.35	-	6.24
	2D	$4s^2$	2	-756.9968	20.68	18.42	17.15	13.06	11.34	10.07	5.31	-	8.46
Ti	5F	$4s^1$	8	-845.3714	21.68	19.43	18.16	13.89	12.18	9.91	5.51	1.45	7.75
	3F	$4s^2$	3	-845.4210	21.68	19.43	18.16	13.98	12.23	11.30	5.52	-	9.67
V	6D	$4s^1$	17	-939.5952	22.68	20.44	19.17	14.78	13.04	11.20	5.61	1.88	8.93
	4F	$4s^2$	8	-939.6375	22.68	20.44	19.17	14.86	13.10	12.36	5.70	5.25	10.62
Cr	7S	$4s^1$	14	-1039.7864	23.68	21.44	20.18	15.64	13.89	12.37	5.67	9.51	10.00
	5D	$4s^2$	17	-1039.7852	23.68	21.44	20.18	15.74	13.95	13.36	5.87	0.93	11.49

Low-level as.-based CI, conf.: $[\text{Ar}] 3d^j 4s^1 4p^k 4d^\ell$, $[\text{Ar}] 3d^j 4s^2 4p^k 4d^\ell$. Green/Blue: Experimental/theor. GS

Algorithm

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- ▶ Efficient exact decomposition into symmetry subspaces
- ▶ Use 1- and 2-body RDM's of wavefunction pairs to represent matrix elements $\langle \Psi_i | H | \Psi_j \rangle$
- ▶ Exact evaluation of Coulomb integrals for STO's (Hankel matrices, Fourier analysis, residue calculus) to build CI Hamiltonian
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Key pts: (i) Many steps done symbolically, (ii) fast algorithm for symm.reduction

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Example (GF, Goddard, Multiscale Model. Simul., 2009)

Minimal asymptotics-based CI for Carbon (paper-and-pencil analysis)

CI space is 70-dimensional (4 valence el's, 8 valence orb's, $70 = \binom{8}{4}$)

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Goal of algorithm: automate such decompositions

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Key pt: Computing time is linear in no. of subshells at fixed ang.mom.cutoff, e.g. $1s, 2s, \dots, ns \sim O(n)$

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$3d^2 4p^2 4d^1$ (2D)	0.036 and 0.038
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Clear evidence of strong, symmetry-reversing, $3d$ - $4d$ inter-shell correlations in Cr, of order of 1 a.u.

List of interesting asymptotic limits

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Isoelectronic limit **atomic ions, N fixed, $Z \rightarrow \infty$**

Hylleraas, Layzer, Wilson, GF/Goddard

Quantum oscillations, shell structure, electron correlation

Thomas-Fermi limit **neutral atoms, $N=Z \rightarrow \infty$**

Lieb, Simon, Scott, Siedentop/Weikard, Hughes, Bach, Fefferman/Seco, Burke

Basic prototype of DFT, averaged semiclassics

Dissociation limit **$|R_A - R_B| \rightarrow \infty$**

London, Casimir/Polder, ...

Leading order van der Waals term not captured by any standard DFT

Coalescence limit **$r_{12} \rightarrow 0$**

Kato, Soerensen et al, N.R.Hill, Kutzelnigg, Goddard

Slow convergence of CI and related expansions

Thermodynamic limit **$N \rightarrow \infty, vol \rightarrow \infty, \frac{N}{vol} = const$**

Lieb, Lebowitz, Thirring, Ceperley/Alder, Lions, Le Bris, Catto, Solovej, Lewin, Cancas, ...

'stability of matter', 'size consistency'

My current other favourite **$\hbar \rightarrow 0$ limit of E_{xc} at fixed ρ**

GF, Cotar, Klueppelberg

Work in progress: leading order term. Novel functional form.

Summary

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Thanks for attention!