Correlation energy of two-electron systems in the high-density limit

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Introduction

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- 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
- Realistic chemistry requires a good treatment of correlation

Some thoughts on electron correlation

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  Wigner Phys Rev 46 (1934) 1002

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- "We conclude that theoretical understanding here lags well behind the power of available computing machinery"
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Can correlation bring electrons closer together?

Coulomb hole in the He atom and H_2 molecule (Coulson & Neilson 1961)

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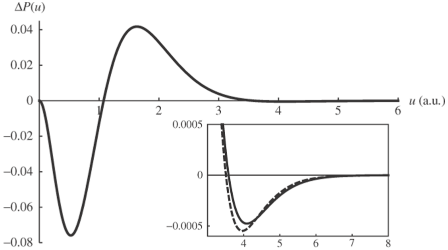

Pearson, Gill, Ugalde & Boyd Mol Phys 107 (2009) 1089

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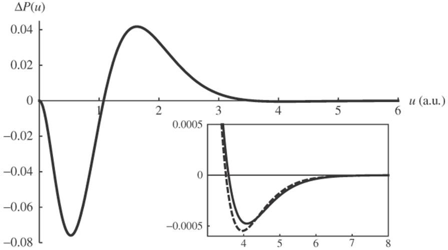

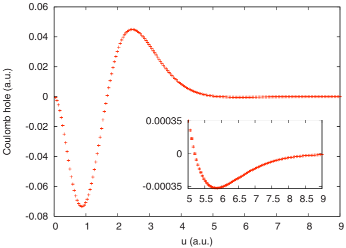

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Per, Russo & Snook J Chem Phys 130 (2009) 134103
See also: Loos & Gill Phys Rev A 81 (2010) 052510

History of accurate calculation on the He atom

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Year	Authors	Energy (a.u.)
1929	Hylleraas	-2.902 43
1957	Kinoshita	-2.903 722 5
1966	Frankowski & Pekeris	-2.903 724 377 032 6
1994	Thakkar & Koga	-2.903 724 377 034 114 4
1998	Goldman	-2.903 724 377 034 119 594
1999	Drake	-2.903 724 377 034 119 596
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2002	Drake et al.	-2.903 724 377 034 119 598 305
2002	Korobov	-2.903 724 377 034 119 598 311 158 7
2006	Schwartz	-2.903 724 377 034 119 598 311 159 245 194 404 440 049 5
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"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."

Schwartz Int J Mod Phys E 15 (2006) 877

The helium-like ions

The Hamiltonian operator

$$\hat{H} = -\frac{1}{2}\left(\nabla_1^2 + \nabla_2^2\right) - Z\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{1}{r_{12}}$$

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

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The $1/Z$ expansion

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$$E = -Z^2 + \frac{5}{8} Z - 0.157666 + O(Z^{-1})$$

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$$E_{\mathrm{HF}} = -Z^2 + \frac{5}{8} Z + \left(\frac{9}{32} \ln \frac{3}{4} - \frac{13}{432} \right) + O(Z^{-1})$$

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- Subtracting yields the analogous correlation energy expansion
$$E_{\text{c}} = -0.046663 + O(Z^{-1})$$
- Thus, in the high-density (*i.e.* $Z \to \infty$), $E_{\text{c}} = -46.7\ \text{mE}_{\text{h}}$

The Hooke's law atom

The Hamiltonian operator

$$\hat{H} = -\frac{1}{2}\left(\nabla_1^2 + \nabla_2^2\right) + Z^4\left(r_1^2 + r_2^2\right) + \frac{1}{r_{12}}$$

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- 1962: Introduced by Kestner and Sinanoglu
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- 2005: Katriel et al. discussed similarities and differences to He atom

The Hooke's law atom

High-density correlation energies

$$E_c(D) = -\frac{\Gamma\left(\frac{D-1}{2}\right)^2}{4\Gamma\left(\frac{D}{2}\right)^2} \sum_{n=1}^{\infty} \frac{\left(\frac{1}{2}\right)_n^2}{\left(\frac{D}{2}\right)_n} \frac{2(1/4)^n - 1}{n!\, n}$$

$$E_c(3) = \frac{2}{\pi}\left[1 + 5\ln 2 - 4\ln\left(1+\sqrt{3}\right)\right] - \frac{1}{3}$$

$$E_c(5) = \frac{8}{27\pi}\left[4 - 3\sqrt{3} + 15\ln 2 - 12\ln\left(1+\sqrt{3}\right)\right] + \frac{7}{27}$$

Loos & Gill J Chem Phys 131 (2009) 241101

The ballium atom

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- 2003: Jung & Alvarellos performed more accurate calculations
- 2010: We obtained near-exact energies for $R = 1$, 5 and 20 bohr
- 2010: We also found that the high-density $E_c = -55.2\ \mathrm{mE_h}$

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- 2009: We examined the analytic properties of its Schrödinger equation
- 2010: We also studied the exact solutions in some special cases
  Loos Phys. Rev. A 81 (2010) 032510

The spherium atom

The spherium atom

Our numerical calculations

First, we solved the Schrödinger equation numerically, e.g.

$R = 1$ $E = 0.852\ 781\ 065\ 056\ 462\ 665\ 400\ 437\ 966\ 038\ 710\ 264\ \ldots$

$R = 100$ $E = 0.005\ 487\ 412\ 426\ 784\ 081\ 726\ 642\ 485\ 484\ 213\ 968\ \ldots$

Loos & Gill Phys Rev A 79 (2009) 062517

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$R = 1 \qquad E = 0.852\,781\,065\,056\,462\,665\,400\,437\,966\,038\,710\,264\ldots$

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Loos & Gill Phys Rev A 79 (2009) 062517

Our analytical calculations

After that, we solved the Schrödinger equation exactly, e.g.

$R = \sqrt{3}/2 \qquad E = 1 \qquad \Psi(\mathbf{r}_1, \mathbf{r}_2) = 1 + r_{12}$

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

Loos & Gill Phys Rev Lett 103 (2009) 123008

The D-spherium atom

Exact solutions of a $(D+1)$-ball

State	D	R	E	$\Psi(\mathbf{r}_1, \mathbf{r}_2)$
^1S	1	$\sqrt{6}/2$	$2/3$	$r_{12}(1 + r_{12}/2)$
	2	$\sqrt{3}/2$	1	$1 + r_{12}$
	3	$\sqrt{10}/2$	$1/2$	$1 + r_{12}/2$
	4	$\sqrt{21}/2$	$1/3$	$1 + r_{12}/3$
^3P	1	$\sqrt{6}/2$	$1/2$	$1 + r_{12}/2$
	2	$\sqrt{15}/2$	$1/3$	$1 + r_{12}/3$
	3	$\sqrt{28}/2$	$1/4$	$1 + r_{12}/4$
	4	$\sqrt{45}/2$	$1/5$	$1 + r_{12}/5$

Loos & Gill Phys Rev Lett 103 (2009) 123008
Loos & Gill Mol Phys (submitted) arXiv:1004.3641v1

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High-density correlation energies

$$E_c(D) = -\frac{\Gamma(D)}{4\pi} \frac{\Gamma\left(\frac{D-1}{2}\right)^2}{\Gamma\left(\frac{D}{2}\right)^2} \sum_{n=1}^{\infty} \frac{(n+1)_{D-2}}{(n+\frac{1}{2})_{D-1}^2} \left[\frac{1}{n} + \frac{1}{n+D-1}\right]$$

$$E_c(2) = 4\ln 2 - 3 \qquad E_c(3) = \tfrac{4}{3} - \tfrac{368}{27}\pi^{-2}$$

$$E_c(4) = \tfrac{64}{75}\ln 2 - \tfrac{229}{375} \qquad E_c(5) = \tfrac{24}{35} - \tfrac{2650112}{385875}\pi^{-2}$$

$$E_c(6) = \tfrac{1024}{2205}\ln 2 - \tfrac{455803}{1389150} \qquad E_c(7) = \tfrac{4924}{10395} - \tfrac{588637011968}{124804708875}\pi^{-2}$$

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D	2	3	4	5	6	7
$-E_c$	0.227411	0.047637	0.019181	0.010139	0.006220	0.004189

Note: For $D = 3$, we find the high-density $E_c = -47.6\ \mathrm{mE_h}$

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A unified view

A unified view

The Hamiltonian

$$\hat{H} = -\frac{1}{2}\left(\nabla_1^2 + \nabla_2^2\right) + V(r_1) + V(r_2) + \frac{1}{r_{12}}$$

A unified view

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The external potentials

Atom	Helium	Spherium	Hookium	Ballium
$V(r)$	$-Z/r$	0	$Z^4 r^2$	$Z^{M+2} r^M$
m	-1	0	2	∞

$$V(r) = \mathrm{sgn}(m) Z^{m+2} r^m$$

A conjecture

Correlation energies (a.u.) in the high-density limit

D	Helium $m=-1$	Spherium $m=0$	Hookium $m=2$	Ballium $m=\infty$
1	$-\infty$	$-\infty$	$-\infty$	$-\infty$
2	-0.220133	-0.227411	-0.239641	-0.266161
3	-0.046663	-0.047637	-0.049703	-0.055176
4	-0.018933	-0.019181	-0.019860	-0.021913
5	-0.010057	-0.010139	-0.010439	-0.011437
6	-0.006188	-0.006220	-0.006376	-0.006940
7	-0.004176	-0.004189	-0.004280	-0.004631
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$

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D	Helium $m=-1$	Spherium $m=0$	Hookium $m=2$	Ballium $m=\infty$
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4	−0.018933	−0.019181	−0.019860	−0.021913
5	−0.010057	−0.010139	−0.010439	−0.011437
6	−0.006188	−0.006220	−0.006376	−0.006940
7	−0.004176	−0.004189	−0.004280	−0.004631
⋮	⋮	⋮	⋮	⋮
∞	$-\frac{\gamma^2}{8} - \frac{67}{384}\gamma^3$	$-\frac{\gamma^2}{8} - \frac{21}{128}\gamma^3$	$-\frac{\gamma^2}{8} - \frac{47}{256}\gamma^3$	$-\frac{\gamma^2}{8} - \frac{53}{128}\gamma^3$

where $\gamma = 1/(D-1)$ is the Kato cusp factor

A conjecture

A precise statement of the conjecture

For the ^1S ground state of two electrons confined by a radial external potential $V(r) = sgn(m) Z^{m+2} r^m$ in D dimension, the high-density correlation energy is

$$\lim_{Z\to\infty} E_{\mathrm{c}}(D,m) \sim -\frac{\gamma^2}{8} + O(\gamma^3)$$

where $\gamma = 1/(D-1)$ is the Kato cusp factor

A proof

In Dudley's footsteps . . .

Herschbach J Chem Phys 84 (1986) 838

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- How can one prove such a conjecture?
- We need to examine the limiting behavior for large Z and D
- This requires double perturbation theory
- After transforming both independent and dependent variables

$$\left(\frac{1}{\Lambda}\hat{\mathcal{T}} + \hat{\mathcal{U}} + \hat{\mathcal{V}} + \frac{1}{Z}\hat{\mathcal{W}}\right)\Phi = \mathcal{E}\Phi$$

where $\Lambda = (D-2)(D-4)/4$

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where $\Lambda = (D-2)(D-4)/4$

- This is now in a suitable form for double perturbation theory

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A proof

In Dudley's footsteps . . .

Goodson & Herschbach J Chem Phys 86 (1987) 4997

A proof

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- We have

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$$\left(\frac{1}{\Lambda}\hat{\mathcal{T}} + \hat{\mathcal{U}} + \hat{\mathcal{V}} + \frac{1}{Z}\hat{\mathcal{W}}\right)\Phi = \mathcal{E}\Phi$$

- In the $D = \infty$ limit, the pure kinetic term $\hat{\mathcal{T}}$ vanishes and we then have a semi-classical electrostatics problem

Goodson & Herschbach J Chem Phys 86 (1987) 4997

A proof

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- In this optimal structure, the angle θ_∞ between the electrons is slightly greater than 90^o
- In the analogous HF calculation, one finds $\theta_\infty = 90^o$ exactly

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In Dudley's footsteps . . .

Loos & Gill Phys Rev Lett (submitted) arXiv:1005.0676v2

A proof

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$$E^{(2)}(D,m) = \left[-\frac{1}{2(m+2)} - \frac{1}{8}\right]\gamma^2 + O(\gamma^3)$$

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- Both of these depend on the external potential parameter m
- But their difference is independent of m, proving the conjecture!

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Take-Home Messages

The state of the art

		Helium	Spherium	Hookium	Ballium
Normal density	E_{HF}		Exact		
	E		Quasi	Quasi	
	E_{c}		Quasi		
High density	E_{HF}	Exact	Exact	Exact	Exact
	E		Exact	Exact	
	E_{c}		Exact	Exact	

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4. High-Z, Large-D: $E_{\mathrm{c}}(\mathrm{He}) = E_{\mathrm{c}}(\mathrm{Sp}) = E_{\mathrm{c}}(\mathrm{Ho}) = E_{\mathrm{c}}(\mathrm{Ba})$

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5. Ultimately, the electron-electron cusp determines everything
6. High-Z, Large-D: $E_c \sim -\gamma^2/8$