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

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23rd June 2010
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PhD & Postdoc

- Yves Bernard (Posmom) & Joshua Hollett (IFT)

Former Postdoc and Research Officer

- Deb Crittenden (Christchurch, NZ) and Andrew Gilbert

Boss (rsc.anu.edu.au/~pgill)

- Peter Gill
Introduction

Why bother with electron correlation?
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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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- The concept was introduced at the dawn of quantum chemistry
  Wigner Phys Rev 46 (1934) 1002
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- There have been recent heroic calculations on the helium atom

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

Coulomb hole in the He atom and H$_2$ molecule (Coulson & Neilson 1961)
Can correlation bring electrons closer together?

Coulomb hole in the He atom and H₂ molecule (Coulson & Neilson 1961)

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See also: Loos & Gill Phys Rev A 81 (2010) 052510
History of accurate calculation on the He atom
History of accurate calculation on the He atom

<table>
<thead>
<tr>
<th>Year</th>
<th>Authors</th>
<th>Energy (a.u.)</th>
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<td>-2.903 724 377 034 119 598 311 159 245 194 404 446 696 905 37</td>
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Pursuit of $E_{\text{He}}$

### History of accurate calculation on the He atom

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“For thousands of years mathematicians have enjoyed competing with one other to compute ever more digits of the number $\pi$. 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.”

The helium-like ions

The Hamiltonian operator

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

- \( Z = 1 \) gives the H\(^-\) anion
- \( Z = 2 \) gives the He atom
- \( Z = 3 \) gives the Li\(^+\) cation
- \( Z = 4 \) gives the Be\(^{2+}\) cation
- etc.
The helium-like ions

The 1/Z expansion
The helium-like ions

The 1/Z expansion

- 1930: During his seminal study of these ions, Hylleraas discovered that

\[ E = -Z^2 + \frac{5}{8}Z - 0.157666 + O(Z^{-1}) \]
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- 1961: Linderberg showed that the analogous HF expansion is

\[ E_{HF} = -Z^2 + \frac{5}{8}Z + \left( \frac{9}{32} \ln \frac{3}{4} - \frac{13}{432} \right) + O(Z^{-1}) \]
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- Subtracting yields the analogous correlation energy expansion
  \[ E_c = -0.046663 + O(Z^{-1}) \]
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The $1/Z$ expansion

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

- Subtracting yields the analogous correlation energy expansion

$$E_c = -0.046663 + O(Z^{-1})$$

- Thus, in the high-density (i.e. $Z \to \infty$), $E_c = -46.7$ mE$_h$
The Hooke’s law atom

The Hamiltonian operator

\[ \hat{H} = -\frac{1}{2} (\nabla_1^2 + \nabla_2^2) + Z^4 (r_1^2 + r_2^2) + \frac{1}{r_{12}} \]
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The Hamiltonian operator

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- 1962: Introduced by Kestner and Sinanoglu
- 1970: White & Byers Brown found the high-density \( E_c = -49.7 \) mE\(_h\)
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- 1989: Kais, Herschbach & Levine found it to be quasi-exactly solvable
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- 2005: Katriel et al. discussed similarities and differences to He atom
The Hooke’s law atom

High-density correlation energies

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

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

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

The ballium atom

The Hamiltonian operator

\[ \hat{H} = -\frac{1}{2} (\nabla_1^2 + \nabla_2^2) + Z^{M+2} (r_1^M + r_2^M) + \frac{1}{r_{12}} \quad (M \approx \infty) \]

The ballium atom

The Hamiltonian operator

$$\hat{H} = -\frac{1}{2} (\nabla_1^2 + \nabla_2^2) + Z^M + 2 (r_1^M + r_2^M) + \frac{1}{r_{12}} \quad (M \approx \infty)$$

- 2002: Introduced by Thompson & Alavi who treated small and large $R$

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- 2010: We also found that the high-density \( E_c = -55.2 \) mE

The spherium atom

The Hamiltonian operator

\[ \hat{H} = -\frac{1}{2} (\nabla_1^2 + \nabla_2^2) + \frac{1}{r_{12}} \]
The spherium atom

The Hamiltonian operator

\[ \hat{H} = -\frac{1}{2} (\nabla^2_1 + \nabla^2_2) + \frac{1}{r_{12}} \]

- 1982: Introduced by Ezra & Berry to model excited states of He atom
The spherium atom

The Hamiltonian operator

$$\hat{H} = -\frac{1}{2} (\nabla_1^2 + \nabla_2^2) + \frac{1}{r_{12}}$$

- 1982: Introduced by Ezra & Berry to model excited states of He atom
- 2007: Seidl used it to study the interaction-strength-interpolation model
The spherium atom

The Hamiltonian operator

\[ \hat{H} = -\frac{1}{2} \left( \nabla_1^2 + \nabla_2^2 \right) + \frac{1}{r_{12}} \]

- 1982: Introduced by Ezra & Berry to model excited states of He atom
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- 2009: We used it as a model system for intracule functional theory (IFT)

Correlation energy of two-electron systems in the high-density limit
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- 2009: We used it as a model system for intracule functional theory (IFT)
- 2009: We examined the analytic properties of its Schrödinger equation
- 2010: We also studied the exact solutions in some special cases

The spherium atom

Our numerical calculations

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

\[ R = 1, \quad E = 0.852781065056462665400437966038710264 \ldots \]

\[ R = 100, \quad E = 0.005487412426784081726642485484213968 \ldots \]


Our analytical calculations

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

\[ R = \sqrt{\frac{3}{2}}, \quad E = 1, \quad \Psi(r_1, r_2) = 1 + r_1^2 \]

\[ R = \sqrt{\frac{7}{2}}, \quad E = 2, \quad \Psi(r_1, r_2) = 1 + r_1^2 + \frac{5}{28} r_2^{12} \]

Loos & Gill Phys Rev Lett 103 (2009) 123008
The spherium atom

Our numerical calculations
First, we solved the Schrödinger equation *numerically*, e.g.

\[ R = 1 \quad E = 0.852 \, 781 \, 065 \, 056 \, 462 \, 665 \, 400 \, 437 \, 966 \, 038 \, 710 \, 264 \ldots \]
\[ R = 100 \quad E = 0.005 \, 487 \, 412 \, 426 \, 784 \, 081 \, 726 \, 642 \, 485 \, 484 \, 213 \, 968 \ldots \]

The spherium atom

Our numerical calculations
First, we solved the Schrödinger equation numerically, e.g.
\[ R = 1 \quad E = 0.852 \ 781 \ 065 \ 056 \ 462 \ 665 \ 400 \ 437 \ 966 \ 038 \ 710 \ 264 \ldots \]
\[ R = 100 \quad E = 0.005 \ 487 \ 412 \ 426 \ 784 \ 081 \ 726 \ 642 \ 485 \ 484 \ 213 \ 968 \ldots \]


Our analytical calculations
After that, we solved the Schrödinger equation exactly, e.g.
\[ R = \sqrt{3}/2 \quad E = 1 \quad \psi(r_1, r_2) = 1 + r_{12} \]
\[ R = \sqrt{7} \quad E = 2/7 \quad \psi(r_1, r_2) = 1 + r_{12} + \frac{5}{28} r_{12}^2 \]

Loos & Gill Phys Rev Lett 103 (2009) 123008
The $D$-spherium atom

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

<table>
<thead>
<tr>
<th>State</th>
<th>$D$</th>
<th>$R$</th>
<th>$E$</th>
<th>$\Psi(r_1, r_2)$</th>
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<tbody>
<tr>
<td>$1S$</td>
<td>1</td>
<td>$\sqrt{6}/2$</td>
<td>$2/3$</td>
<td>$r_{12}(1 + r_{12}/2)$</td>
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<td>2</td>
<td>$\sqrt{3}/2$</td>
<td>1</td>
<td>$1 + r_{12}$</td>
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<td>3</td>
<td>$\sqrt{10}/2$</td>
<td>$1/2$</td>
<td>$1 + r_{12}/2$</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>$\sqrt{21}/2$</td>
<td>$1/3$</td>
<td>$1 + r_{12}/3$</td>
</tr>
<tr>
<td>$3P$</td>
<td>1</td>
<td>$\sqrt{6}/2$</td>
<td>$1/2$</td>
<td>$1 + r_{12}/2$</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>$\sqrt{15}/2$</td>
<td>$1/3$</td>
<td>$1 + r_{12}/3$</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>$\sqrt{28}/2$</td>
<td>$1/4$</td>
<td>$1 + r_{12}/4$</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>$\sqrt{45}/2$</td>
<td>$1/5$</td>
<td>$1 + r_{12}/5$</td>
</tr>
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Loos & Gill Phys Rev Lett 103 (2009) 123008
Loos & Gill Mol Phys (submitted) arXiv:1004.3641v1
The $D$-spherium atom

High-density correlation energies

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

$$E_c(2) = 4 \ln 2 - 3$$
$$E_c(3) = \frac{4}{3} - \frac{368}{27} \pi^{-2}$$
$$E_c(4) = \frac{64}{75} \ln 2 - \frac{229}{375}$$
$$E_c(5) = \frac{24}{35} - \frac{2650112}{385875} \pi^{-2}$$
$$E_c(6) = \frac{1024}{2205} \ln 2 - \frac{455803}{1389150}$$
$$E_c(7) = \frac{4924}{10395} - \frac{588637011968}{124804708875} \pi^{-2}$$

The $D$-spherium atom

High-density correlation energies

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

<table>
<thead>
<tr>
<th>$D$</th>
<th>$E_c$</th>
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<tr>
<td>2</td>
<td>0.227411</td>
</tr>
<tr>
<td>3</td>
<td>0.047637</td>
</tr>
<tr>
<td>4</td>
<td>0.019181</td>
</tr>
<tr>
<td>5</td>
<td>0.010139</td>
</tr>
<tr>
<td>6</td>
<td>0.006220</td>
</tr>
<tr>
<td>7</td>
<td>0.004189</td>
</tr>
</tbody>
</table>

Note: For $D = 3$, we find the high-density $E_c = -47.6 \text{ mE}_h$

A unified view
A unified view

The Hamiltonian

\[ \hat{H} = -\frac{1}{2} (\nabla_1^2 + \nabla_2^2) + V(r_1) + V(r_2) + \frac{1}{r_{12}} \]
A unified view

The Hamiltonian

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The external potentials

<table>
<thead>
<tr>
<th>Atom</th>
<th>Helium</th>
<th>Spherium</th>
<th>Hookium</th>
<th>Ballium</th>
</tr>
</thead>
<tbody>
<tr>
<td>(V(r))</td>
<td>(-Z/r)</td>
<td>0</td>
<td>(Z^4 r^2)</td>
<td>(Z^{M+2} r^M)</td>
</tr>
<tr>
<td>(m)</td>
<td>-1</td>
<td>0</td>
<td>2</td>
<td>(\infty)</td>
</tr>
</tbody>
</table>

\[V(r) = \text{sgn}(m)Z^{m+2} r^m\]
A conjecture

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

<table>
<thead>
<tr>
<th>$D$</th>
<th>Helium $m = -1$</th>
<th>Spherium $m = 0$</th>
<th>Hookium $m = 2$</th>
<th>Ballium $m = \infty$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$-\infty$</td>
<td>$-\infty$</td>
<td>$-\infty$</td>
<td>$-\infty$</td>
</tr>
<tr>
<td>2</td>
<td>$-0.220133$</td>
<td>$-0.227411$</td>
<td>$-0.239641$</td>
<td>$-0.266161$</td>
</tr>
<tr>
<td>3</td>
<td>$-0.046663$</td>
<td>$-0.047637$</td>
<td>$-0.049703$</td>
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## A conjecture

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

<table>
<thead>
<tr>
<th>$D$</th>
<th>Helium ($m = -1$)</th>
<th>Spherium ($m = 0$)</th>
<th>Hookium ($m = 2$)</th>
<th>Ballium ($m = \infty$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$-\infty$</td>
<td>$-\infty$</td>
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</tr>
<tr>
<td>2</td>
<td>$-0.220133$</td>
<td>$-0.227411$</td>
<td>$-0.239641$</td>
<td>$-0.266161$</td>
</tr>
<tr>
<td>3</td>
<td>$-0.046663$</td>
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<tr>
<td>$\infty$</td>
<td>$-\gamma^2 / 8 - 67 \gamma^3 / 384$</td>
<td>$-\gamma^2 / 8 - 21 \gamma^3 / 128$</td>
<td>$-\gamma^2 / 8 - 47 \gamma^3 / 256$</td>
<td>$-\gamma^2 / 8 - 53 \gamma^3 / 128$</td>
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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 $V(r) = \text{sgn}(m)Z^{m+2}r^m$ in $D$ dimension, the high-density correlation energy is

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

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

In Dudley’s footsteps . . .

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- How can one prove such a conjecture?

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\left(\frac{1}{\Lambda} \hat{T} + \hat{U} + \hat{V} + \frac{1}{Z} \hat{W}\right) \Phi = \varepsilon \Phi
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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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- In this optimal structure, the angle $\theta_\infty$ between the electrons is slightly greater than $90^\circ$

- In the analogous HF calculation, one finds $\theta_\infty = 90^\circ$ exactly

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- Now, by carefully taking the high-Z limit, one finds

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

## Take-Home Messages

### The state of the art

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<tr>
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<th>Helium</th>
<th>Spherium</th>
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<tbody>
<tr>
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</tr>
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<td>$E$</td>
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<td></td>
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<table>
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6. High-Z, Large-\( D \): \( E_c \sim -\gamma^2/8 \)