A tale of two electrons: correlation at high density

Pierre-François Loos and Peter M. W. Gill
Research School of Chemistry, Australian National University, Canberra, Australia
email: {loos,gill}@rsc.anu.edu.au
website: http://rsc.anu.edu.au/∼{loos,pgill}

Why bother with electron correlation?

- HF theory ignores correlation and gives 99% of the energy
- 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

- The concept was introduced at the dawn of quantum chemistry
  Wigner Phys Rev 46 (1934) 1002
- Its definition was agreed somewhat later
  Löwdin Adv Chem Phys 2 (1959) 207
- One Nobel Laureate used to refer to it as "the stupidity energy"
  Feynmann (1972)
- There have been recent heroic calculations on the helium atom
  Nakashima & Nakatsuji J Chem Phys 127 (2007) 224104
- "We conclude that theoretical understanding here lags well behind the power of available computing machinery"
  Schwartz Int J Mod Phys E 15 (2006) 877

The helium-like ions [1]

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

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

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

- 1961: Linderberg showed that the analogous HF expansion is

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

- Subtracting yields the analogous correlation energy expansion

$$E_{\text{c}} = -0.046663 + O(Z^{-1})$$

- Thus, in the high-density (*i.e.* $Z \to \infty$),

$$E_{\text{c}} = -46.7 \text{ mE}_{\text{h}}$$

The Hooke's law atom [1]

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

- 1962: Introduced by Kestner and Sinanoglu
- 1970: White & Byers Brown found the high-density

$$E_{\text{c}} = -49.7 \text{ mE}_{\text{h}}$$

- 1989: Kais, Herschbach & Levine found it to be quasi-exactly solvable
- 1993: Taut found an infinite set of solutions
- 2005: Katriel et al. discussed similarities and differences to He atom
- 2009: We found [1]

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

The ballium atom [2]

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

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

$$E_{\text{c}} = -55.2 \text{ mE}_{\text{h}}$$

The spherium atom [3-7]

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

- 1982: Introduced by Ezra & Berry to model excited states of He atom
- 2007: Seidl used it to study the interaction-strength-interpolation model
- 2009: We used it as a model system for intracule functional theory (IFT) [6]
- 2009: We examined the analytic properties of its Schrödinger equation [4,7]
- 2009: We also found that the high-density [1]

$$E_{\text{c}} = -47.6 \text{ mE}_{\text{h}}$$

- 2009: ... and the more general formula [1]

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

- 2010: We also studied the exact solutions in some special cases [5]

Quasi-exact solutions of spherium [4,7]

State	D	R	E	$\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2)$
^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	$1 + r_{12}/5$

A Conjecture [1]

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
⋮	⋮	⋮	⋮	⋮
∞	$-\frac{\gamma^2}{8} - \frac{67}{384}\gamma^3$	$-\frac{\gamma^2}{8} - \frac{21}{128}\gamma^3$	$-\frac{\gamma^2}{8} - \frac{47}{256}\gamma^3$	$-\frac{\gamma^2}{8} - \frac{53}{128}\gamma^3$

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

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

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

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

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

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

A Proof [8]

- 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 $\Lambda = (D-2)(D-4)/4$
Herschbach J Chem Phys 84 (1986) 838

- In the $D = \infty$ limit, the pure kinetic term $\hat{\mathcal{T}}$ vanishes and we then have a semi-classical electrostatics problem
- The electrons settle into a fixed "Lewis" structure that minimizes $\hat{\mathcal{U}} + \hat{\mathcal{V}} + \frac{1}{Z}\hat{\mathcal{W}}$
- 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

Goodson & Herschbach J Chem Phys 86 (1987) 4997

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

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

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

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

Conclusions

- The high-density limit sheds light on the normal case
- High-Z:

$$E_{\text{c}}(\text{He}) \approx E_{\text{c}}(\text{Sp}) \approx E_{\text{c}}(\text{Ho}) \approx E_{\text{c}}(\text{Ba})$$

- The high-dimension limit sheds light on these cases
- High-Z, Large-D:

$$E_{\text{c}}(\text{He}) = E_{\text{c}}(\text{Sp}) = E_{\text{c}}(\text{Ho}) = E_{\text{c}}(\text{Ba})$$

- Ultimately, the electron-electron cusp determines everything
- High-Z, Large-D: $E_{\text{c}} \sim -\gamma^2/8$

References

[1] P.-F. Loos and P. M. W. Gill, *J. Chem. Phys.* **131** (2009) 241101.
[2] P.-F. Loos and P. M. W. Gill, *J. Chem. Phys.* **132** (2010) 234111.
[3] P.-F. Loos and P. M. W. Gill, *Phys. Rev. A* **79** (2009) 062517.
[4] P.-F. Loos and P. M. W. Gill, *Phys. Rev. Lett.* **103** (2009) 123008.
[5] P.-F. Loos, *Phys. Rev. A* **81** (2010) 032510.
[6] P.-F. Loos and P. M. W. Gill, *Phys. Rev. A* **81** (2010) 052510.
[7] P.-F. Loos and P. M. W. Gill, *Mol. Phys.* (2010) submitted.
[8] P.-F. Loos and P. M. W. Gill, *Phys. Rev. Lett.* (2010) submitted.