Something you didn't know: *all molecules are the same!*

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Outline

- Stability of matter.
- Scaled energy/bond length relation, asymptotic behaviour.
- Numerical tests 1: behaviour with nuclear charge.
- Numerical tests 2: homologous series.
- Conclusions.

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- Original paper: NG, JPS, PRT, *Int J Quantum Chem*, **111**, 3324 (2011).

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- Matter would not collapse without PP, but correct scaling with Z and N would not follow.
- Bosonic matter would follow a $-N^{7/5}$ law.

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- "Dyson-Lenard proof one of the most difficult up to that time in the math phys literature" (Lieb).
- Simplified by Lieb and Thirring in 1975 using properties of Thomas-Fermi theory.
- Other issues arising from incorporation of relativity and of magnetic fields. Does not incorporate gravity (which of course *can* cause collapse).

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- Polyatomic case can be “collapsed” to the diatomic limit.

$$\begin{aligned} H &= -\frac{1}{2}\sum_i \nabla_i^2 + \sum_{i>j} r_{ij}^{-1} - \sum_{i,A} Z_A r_{iA}^{-1} + \sum_{A>B} Z_A Z_B R_{AB}^{-1} \\ &\to -\frac{1}{2}\sum_i \nabla_i^2 + \sum_{i>j} r_{ij}^{-1} - \sum_{i,A} Z_A r_{iA}^{-1} + Z_A Z_B R_{AB}^{-1} \end{aligned}$$

but not further! (Must keep nuclear repulsion term.)

Behaviour of the exact energy

- Let the nuclear charges be $Z_1 e$ and $Z_2 e$ and let $Z = Z_1 + Z_2$. Total energy is E.
- Separated atom energies are E_1 and E_2.
- Define the scaled internuclear distance $\rho = Z^{\frac{1}{3}} R$.
- Then (Lieb, Simon) as $Z \to \infty$, for finite ρ, all diatomic potential curves have the same leading term,

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- Leading term is in fact the Thomas-Fermi (TF) energy.

Thomas-Fermi energy

- Simple statistical model:

$$E_{TF} = E_{NR} + C\int [n(r)]^{5/3}\,dr + \int n(r)V_{NA}(r)dr + \frac{1}{2}\int\int \frac{n(r)n(r')}{|r-r'|}drdr'$$

$n(r)$ is the electron density, V_{NA} is the nuclear attraction, and E_{NR} is the nuclear repulsion energy.

Behaviour of the Hartree-Fock energy

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- Exactly the same as the exact energy!
- Simply put, both the exact and Hartree-Fock energies have the same leading term — which is the TF energy — as $Z \to \infty$, for finite ρ.
- This includes $\rho = 0$.
- Also shown for a model with a relativistic kinetic energy operator and for next-higher terms in the energy expansion.

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- Not so!
- Consider for simplicity a homonuclear diatomic. Then $Z_1 Z_2 / R = 1/4\rho$ (certainly the same for all such diatomics).
- Define now $E_{\text{elec}} = E - Z_1 Z_2 / R$ and $\mathscr{E}_{\text{elec}} = Z^{-\frac{7}{3}} (E_{\text{elec}} - E_1 - E_2)$.
- Identical behaviour for different diatomics means identical $\mathscr{E}_{\text{elec}}$, not just that the latter is overwhelmed by the nuclear repulsion.

Not trivial, then, but good for what?

- Any known analytical behaviour is useful to calibrate and improve our methods.
- E.g., improving basis sets, or designing functionals in DFT.
- (Accepted, some analytical behaviour is useless, like asymptotic decay of density/orbitals in atoms.)

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Computational tests

- Can use Hartree-Fock since behaviour is the same as the exact energy.
- Not difficult to approach HF limit with modern basis sets.
- Must be prepared to approach/describe united-atom (UA) limit.
- Choose a variety of diatomics covering a range of Z (for simplicity, homonuclear diatomics with ${}^1\Sigma_g^+$ ground states), study R values inwards towards UA limit.

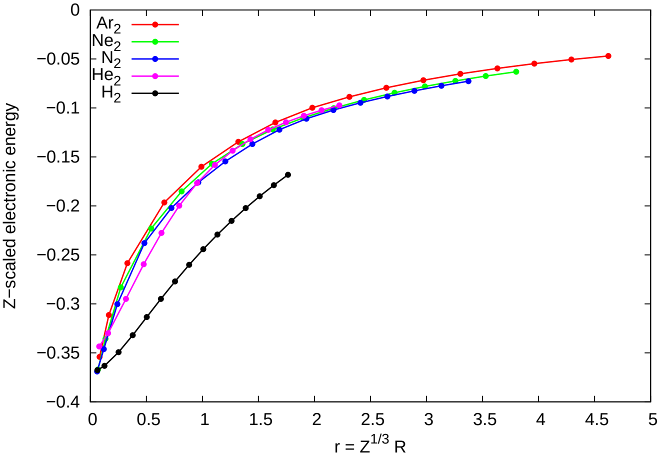
Computational methods

- Can't do much *ab initio* that's simpler than Hartree-Fock!
- Use correlation-consistent basis sets: cc-pCVQZ but only up to $l+2$ for the given atoms. (E.g., no g functions for N.)
- Large even-tempered spd or $spdf$ set at bond midpoint. At small R a lot of linear dependence — canonical orthonormalization. No problems envisaged with BSSE this far up repulsive wall.
- Follow the lowest $^1\Sigma_g^+$ curve throughout (no idea if this remains the ground state for all $R \to 0$, of course).
- H_2, He_2, N_2, Ne_2, Ar_2.

Computational methods

- Some potential wave function issues. HF UA for H_2 lowest $^1\Sigma_g^+$ state is He $1s^2$ ground state, but this is not true for UAs of the other diatomics.
- Use CASSCF with minimal active space needed for smooth transition to UA lowest "closed shell" (can be mixed like N_2 goes to Si $(^1D + {}^1S)$).
- In practice see wave functions dominated by a single configuration in to short R, then rapid transition to UA single configuration. (He_2 transition to Be not observed at distances used.)
- All calculations performed with Dalton.

Diatomic curves (a.u.)



Distance comparisons (a_0)

	H_2	He_2	N_2	Ne_2	Ar_2
ρ	R	R	R	R	R
5.001			2.075		
1.765	1.4011				
1.5	1.191	0.945	0.622	0.553	0.454
1.0	0.794	0.630	0.415	0.368	0.303
0.5	0.397	0.315	0.207	0.184	0.151

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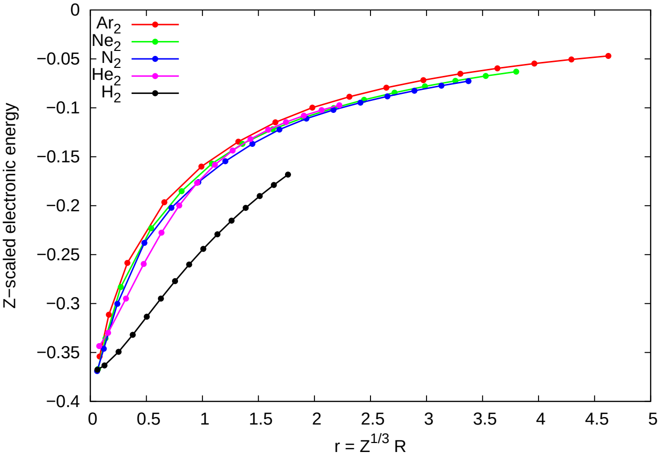

Observations

- Not unexpectedly, H_2 is exceptional.
- He_2 behaves somewhat oddly at very short distances (possibly anticipating the transition to UA).
- The other three show essentially the same behaviour, basically to within mE_h, at all ρ values studied.
- Convergence to large Z behaviour appears exceptionally rapid, and is observed at relatively large ρ or R values.

Further tests

- The molecules examined are quite different in character: either strongly bonded, or not at all (in HF — very TF-like).
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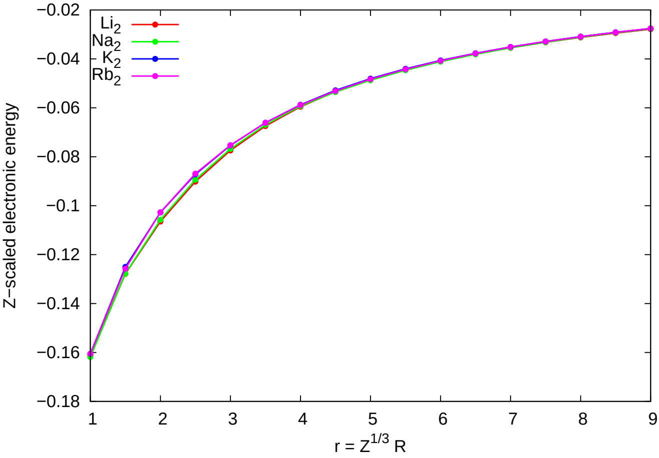
- Bound molecules that are "plausible" TF candidates?
- Alkali-metal dimers. Noble gas-like cores inside a weak bonding pair.
- HF calculations on Li_2, Na_2, K_2, Rb_2. No bond functions, no CASSCF, as ultra-small R values not considered.

Alkali-metal dimers (a.u.)



Distance comparisons (a_0)

	Li_2	Na_2	K_2	Rb_2
ρ	R	R	R	R
9.0	4.953	1.768	0.526	0.125
7.0	3.852	1.375	0.409	0.097
5.0	2.752	0.982	0.292	0.070
3.0	1.651	0.589	0.175	0.042

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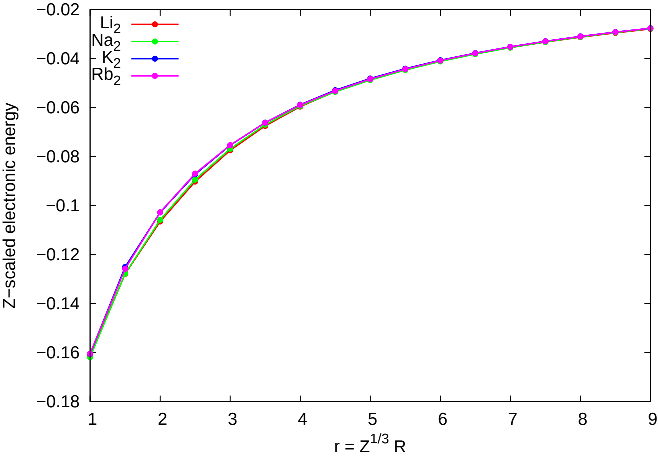

Observations

- Again concordant to mE_h level, at relatively large ρ values (almost to R_e in Li_2!).
- Some divergence at ρ values between 2 and 3.
- Actual binding energies are rather small and badly underestimated by HF, which is partly responsible for similarity of curves for larger ρ: $\mathscr{E}_\mathrm{elec}$ itself is becoming small.

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- Large Z behaviour observed at remarkably large ρ values.
- Note that the mathematics does not *exclude* that possibility: simply not proven (yet?).
- $\mathscr{E}_{\mathrm{elec}}$ looks like a quantity that could be used to decide whether certain parametrized methods are realistic or not (proposed in first paper).
- Not really. In the intervening years: DFT, correlated methods, heteronuclear diatomics, open-shell systems — all show the same behaviour.