Relativistic corrections to Schrödinger's equation based on the Zeroth Order Regular Approximation

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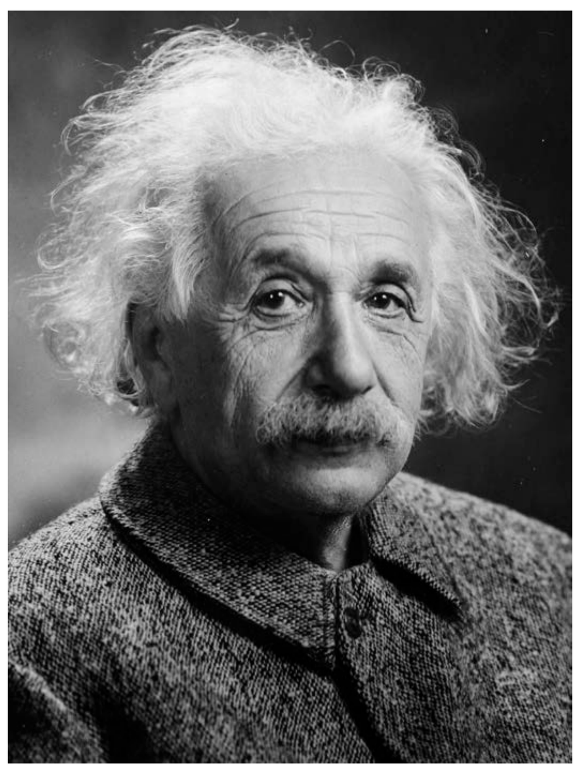
Introduction

- The equations of quantum mechanics have been known for close to 100 years now, however, in most cases of interest, they are too difficult to solve analytically (i.e. with pen and paper), so a computational approach is necessary.
- When studying heavy elements (e.g. lead) there is the added difficulty of including effects arising from Einstein's theory of relativity.
- Heavy elements are important for their use in technologies such as smart phone touchscreens (where Indium tin oxide is used), so being able to model their properties computationally (as opposed to experimentally) is of great interest [1].
- Relativity affects both the structure of a molecule, and its spectroscopic properties [2].



Aims

- Relativistic quantum calculations typically incur a far greater computational workload than the corresponding non-relativistic calculation, therefore a method for quantum calculations that includes relativistic effects, at a comparable computational cost to the non-relativistic case is sought.
- To alleviate problems of gauge invariance in the Zeroth Order Regular Approximation (ZORA) method.

ZORA Method

- One of the most promising methods for achieving the first aim is the ZORA method [3,4].
- When considering structure, valence (high level) electrons are the most important, as these control bonding. ZORA provides a high level of both speed and accuracy when considering these states [4].
- An issue that arises when using ZORA is that it is not 'gauge invariant' (i.e. a constant shift in the potential does not lead to a constant shift of the energy), so an expansion of the potential is sought that will negate this problem (see implementation) [5].

Implementation

- The ZORA equations were implemented into a spherically symmetric hydrogenic atom code using a Slater function basis set, ψ.
- When calculating ZORA energies, the kinetic energy matrix elements are given by:

$$T_{ij} = \left\langle \frac{\partial \psi_i}{\partial r} \middle| \frac{c^2}{2c^2 - V} \middle| \frac{\partial \psi_j}{\partial r} \right\rangle$$

- 'Scaled ZORA' energies were also calculated, in the case of a hydrogenic atom, these energies exactly match those analytically derived from the Dirac equation [4]. They are related to the standard ZORA energies by:

$$E^{scaled} = \frac{E^{ZORA}}{1 + \left\langle \Phi^{ZORA} \middle| P \frac{c^2}{(2c^2 - V)^2} P \middle| \Phi^{ZORA} \right\rangle}$$

- The potential was expanded in a 'telescopic' expansion of Gaussian functions, G:

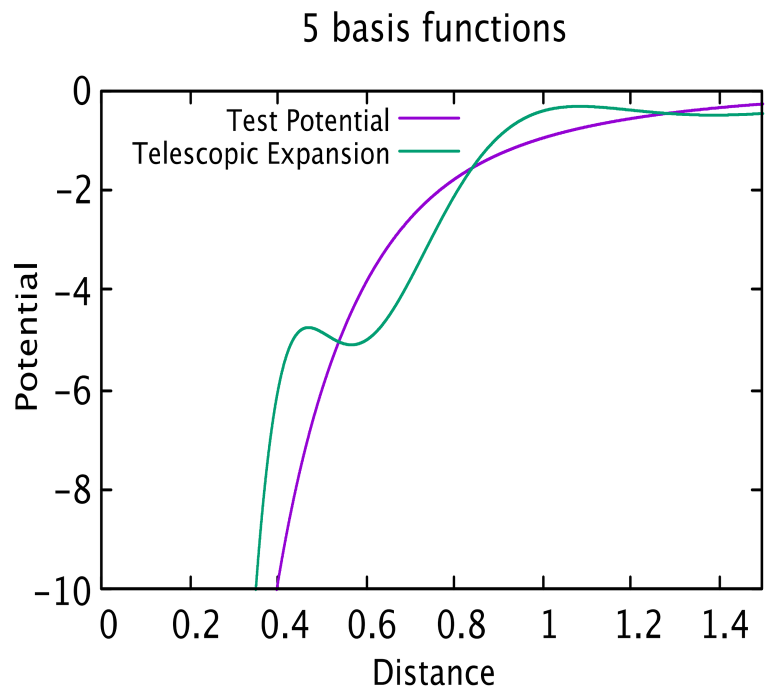
$$G_0(r) = \left(\frac{\alpha_0}{\pi}\right)^{\frac{3}{2}} e^{-\alpha_0 r^2}$$

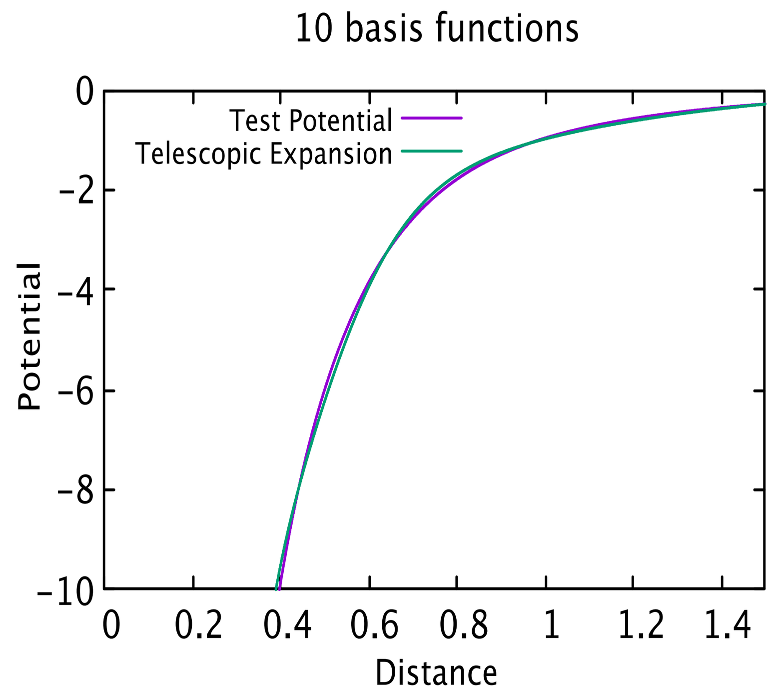
$$G_i(r) = \left(\frac{\alpha_i}{\pi}\right)^{\frac{3}{2}} e^{-\alpha_i r^2} - \left(\frac{\alpha_{i-1}}{\pi}\right)^{\frac{3}{2}} e^{-\alpha_{i-1} r^2}$$

- G_0 integrates to 1, and so carries the norm, while all other G_i integrate to zero, thus carrying the gauge.
- It is proposed then that use of this telescopic expansion will dramatically improve the gauge issues typically associated with the ZORA method.

Results

Orbital	Dirac	ZORA	ZORA (van Lenthe)	Scaled ZORA	Scaled ZORA (van Lenthe)
1s	-4861.2	-5583.9	-5583.9	-4861.2	-4861.2
2s	-1257.39	-1300.95	-1300.95	-1257.39	-1257.39
3s	-539.09	-546.94	-546.94	-539.09	-539.09
4s	-295.257	-297.529	-297.597	-295.182	-295.257
5s	-185.485	-185.901	-186.405	-184.963	-185.485
6s	-127.093	-125.942	-127.525	-125.469	-127.093
7s	-92.441	-89.923	-92.669	-92.669	-92.441





Conclusion

- Results have been shown to match previous ZORA calculations [4].
- It was also shown that the potential (purple) can be decomposed in a telescopic expansion (green).

Further Work

- Implement this atomic code into a full molecular code.
- Test potentials expressed in the Gaussian basis set for gauge invariance.

References

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