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.

Relativity affects both the structure of a molecule, and its spectroscopic properties.

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

| Anthony Sweeting*, 150380401, a.sweeting1@newcastle.ac.uk | Theoretical Physics Bsc Honours | School of Maths, Stats and Physics | Supervisor: Dr Mark Rayson |

Introduction

The ZORA equations were implemented into a spherically symmetric hydrogenic atom code using a Slater function basis set, \( \psi \).

When calculating ZORA energies, the kinetic energy matrix elements are given by:

\[
T_{ij} = \frac{\hbar^2}{2m} \left( \frac{\partial^2 \psi_i}{\partial r^2} \right) \left( \frac{\partial^2 \psi_j}{\partial r^2} \right)
\]

‘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:

\[
E_{\text{scaled}} = E_{\text{ZORA}} \left( \frac{1}{1 + \langle \Phi_{\text{ZORA}} | \rho | \Phi_{\text{ZORA}} \rangle} \right)
\]

The potential was expanded in a ‘telescopic’ expansion of Gaussian functions, \( G_i \):

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

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

\( G_0 \) 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.

Implementation

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