Using Hydrogenic Orbitals to Improve DFT

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1. Introduction

- Density Functional Theory (DFT) is rooted in the Hohenberg-Kohn theorem, which states that the external potential is a functional of the density [1]. This theorem allows us to map the interacting system to a fictitious non-interacting Kohn-Sham system, with an effective one-body potential, that reproduces the groundstate density of the interacting system [2]. Formally, this mapping is exact, which suggests that studying the non-interacting system may provide useful insight into the interacting system. The Bohr atom is such a system, with non-interacting electrons whose orbitals are hydrogenic. Unlike the real atom, the Bohr atom's n-shells are filled sequentially (e.g. *3d* is filled before *4s*).

- **We use the Bohr atom as a model to find the asymptotic expansion of its exchange energy E_X in a charge-neutral scaling of atomic number $Z \to \infty$.** Asymptotic expansions of this kind have been found for the kinetic energy of the real atom [3] and the exchange energy of the real atom [4]. It is important that functionals used in DFT reproduce the correct coefficients in this limit. Knowledge of these coefficients enables us to test new functionals as well as derive parameters used in functionals non-empirically by enforcing the correct asymptotic expansion [4].

- **We have also developed a new piecewise smooth model for the density of the Bohr atom that improves upon the Thomas-Fermi density.** We calculate how much our model improves the exchange energy under the PBE exchange functional.

2. Asymptotic Expansions

- In charge-neutral scaling, the number of electrons N is increased by a factor ζ: $N \to \zeta N$. The external potential is also scaled by ζ according to

$$v_{ext}^{\zeta} = \zeta^{4/3} v_{ext}(\zeta^{1/3} r), \tag{1}$$

in order to preserve the neutrality of the atom.

- Under this scaling, the exchange energy can be expanded in powers of $Z^{1/3}$

$$E_{\rm X} = c_0 Z^{5/3} + c_1 Z^{4/3} + c_2 Z + \ldots \tag{2}$$

where the leading coefficient c_0 is given exactly by LDA applied to the Thomas-Fermi density [5, 6, 7]. **The $Z^{4/3}$ term is thought not to exist [8], but we will investigate whether or not this is true and we will try to extract c_2 for the Bohr atom.**

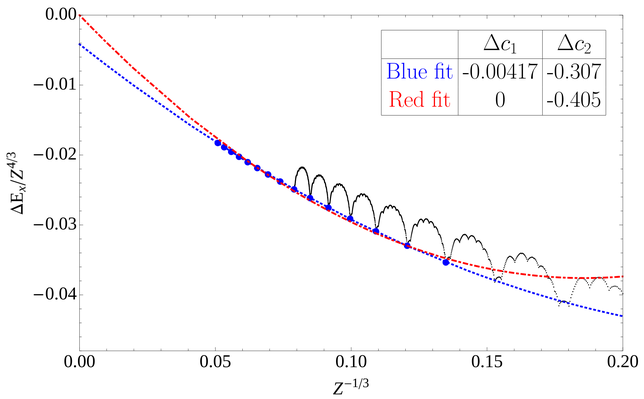
3. Extracting Coefficients

- We have calculated the exact exchange energy of the Bohr atom out to $Z = 7590$. To extract the coefficients in the asymptotic expansion, we subtract off the LDA exchange energy and divide by $Z^{4/3}$

$$\frac{\Delta E_{\rm X}}{Z^{4/3}} = \frac{E_{\rm X} - E_{\rm X}^{\rm LDA}}{Z^{4/3}} = \Delta c_1 + \Delta c_2 Z^{-1/3} + \ldots \tag{3}$$

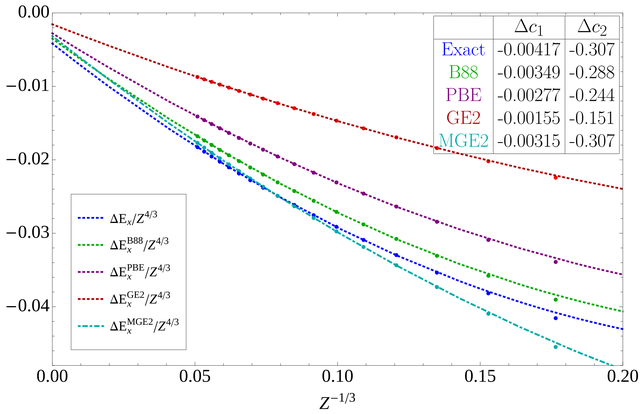
where $\Delta c_i = c_i - c_i^{\rm LDA}$. This removes the leading term and reduces the amplitude of oscillations due to shell structure. We estimate that $0 \geq c_1^{\rm LDA} \geq -0.000345$ and $c_2^{\rm LDA} \approx -0.1$.

- Fig. 1 shows Eq. 3 plotted versus $Z^{-1/3}$, and the table gives the coefficients for the red and blue fits. **Because our results are sensitive to the parameters of the fit, it is possible that $\Delta c_1 = 0$.** We estimate that $-0.00417 \leq \Delta c_1 \leq 0$ and $-0.5 \leq \Delta c_2 \leq -0.3$.



	Δc_1	Δc_2
Blue fit	-0.00417	-0.307
Red fit	0	-0.405

Figure 1: Extracting asymptotic coefficients for the exact exchange energy: the dashed lines are quadratic fits to the last 15 blue dots ($408 \leq Z \leq 7590$), which are the closed n-shell configurations. The constant term of the fit gives Δc_1 while the coefficient of the linear term is Δc_2. The red dashed line has the constant term Δc_1 set to 0.



	Δc_1	Δc_2
Exact	-0.00417	-0.307
B88	-0.00349	-0.288
PBE	-0.00277	-0.244
GE2	-0.00155	-0.151
MGE2	-0.00315	-0.307

Figure 2: Extracting asymptotic coefficients for some common exchange functionals: the dashed lines are quadratic fits to the last 15 dots ($408 \leq Z \leq 7590$), which are the closed n-shell configurations. The constant term of the fit gives Δc_1 while the coefficient of the linear term is Δc_2.

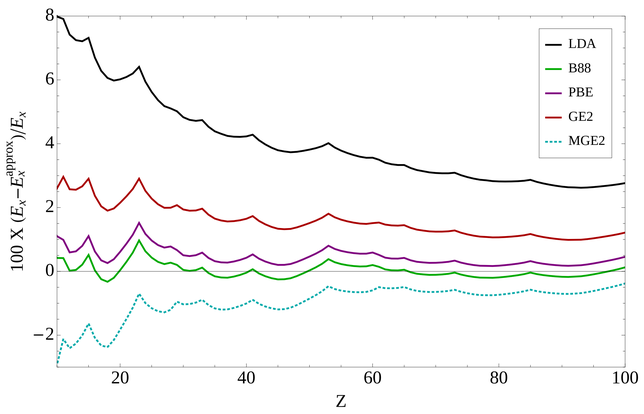


Figure 3: The percentage error of some common exchange functionals evaluated on the exact Bohr atom density.

4. Comparison with Common Functionals

- In Fig. 2, we plot $\Delta E_{\rm X}/Z^{4/3}$ versus $Z^{-1/3}$ for several different common exchange functionals, including two Generalized Gradient Approximation functionals, B88 and PBE, and the second-order Gradient Expansion Approximation, GE2. We use the same procedure in order to extract the asymptotic coefficients, shown in the table in Fig. 2. These results are the same as those for the interacting atom [4]: **B88 and PBE are very close to having the correct asymptotic form, while GE2 is off by a factor of 2.**

- To see why these asymptotic expansions are useful, **we can create a modified second-order Gradient Expansion Approximation (MGE2) by altering its parameter to give the correct coefficients.** Fig. 3 shows the percentage error for each exchange functional for $10 \leq Z \leq 100$. It is clear that MGE2 approaches zero percent error faster than GE2.

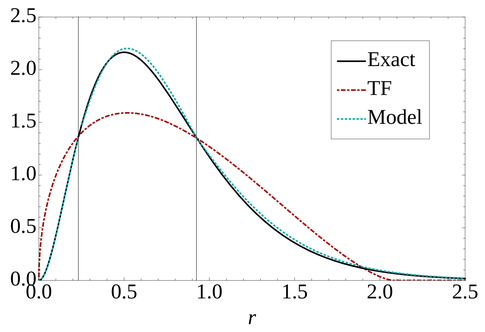
5. Extension of Thomas-Fermi Density

- Lieb modeled the density of the real atom by dividing it into five regions [9]. Instead, we divide it into three regions (shown in Fig. 4 for Helium), partitioned by the first and last intersections of the Thomas-Fermi density with the exact density. Our model is based on Kato's cusp condition, Lieb and Heilmann's limiting function for the exact hydrogenic density as $Z \to \infty$ [10], and Koopman's ionization potential.

- **The table in Fig. 4 shows that the model density yields a much more accurate exchange energy than does the Thomas-Fermi density.**

	Exact	TF	Model
$E_{\rm X}^{\rm PBE}$	-1.223	-1.353	-1.245
$E_{\rm X}^{\rm exact}$		-1.25	

Figure 4: Our 3-region model captures the quantum correction to the Thomas-Fermi density in the Bohr atom as well as the correct limiting behavior as $r \to 0$ and $r \to \infty$.



6. Conclusion

- There is still some uncertainty in the values of the asymptotic coefficients, as we do not have enough data points to accurately determine them. Schwinger derived the first two corrections to the leading coefficient in the asymptotic expansion of the total energy [5, 11], **so it might possible to apply his same method to the exchange energy in order to analytically determine these coefficients.**

- Nonetheless, we have demonstrated the usefulness of these coefficients in modifying GE2 to have the correct asymptotic expansion. **This helps to explain why GGAs were necessary to improve upon GE2 and obtain the correct asymptotic expansion.**

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