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The Liu-Parr power series expansion of the Pauli kinetic energy functional with the incorporation of shell-inducing traits: Atoms

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Abstract

An approximate expression for the Pauli kinetic energy functional T_p is advanced in terms of the Liu-Parr expansion [S. Liu, R.G. Parr, *Phys. Rev. A* **1997**, 55, 1792] which involves a power series of the one-electron density. We use this explicit functional for T_p to compute the value of the noninteracting kinetic energy functional T_s of 34 atoms, from Li to Kr (and their positive and negative monoions). In particular, we examine the effect that a shell-by-shell mean-square optimization of the expansion coefficients has on the kinetic energy values and explore the effect that the size of the expansion, given by the parameter n , has on the accuracy of the approximation. The results yield a mean absolute percent error $\Delta_{\text{abs}} = (1/N) \sum_{i=1}^N \Delta_i$ for 34 neutral atoms of 0.15, 0.08, 0.04, 0.03, and 0.01 for expansions with $n = 3, 4, 5, 6$, and 7, respectively (where $\Delta_i = 100 |T_s^{\text{app}}(i) - T_s^{\text{HF}}(i)| / T_s^{\text{HF}}(i)$). We show that these results, which are the most accurate ones obtained to date for the representation of the noninteracting kinetic energy functional, stem from the imposition of shell-inducing traits. We also compare these Liu-Parr functionals with the exact but nonexplicit functional generated in the local-scaling transformation version of DFT.

KEYWORDS

density functional theory, enhancement factor, kinetic energy functional, Kohn-Sham, Pauli functional

1 | INTRODUCTION

An important and long-enduring problem in the quantum mechanical description of many-particle systems is how to represent adequately the noninteracting kinetic energy, $T_s[\rho]$, as a functional of the one-particle density.^[1–3] In the early development of quantum theory, such as is embodied in the Thomas-Fermi approximation, the kinetic energy was given as a functional of ρ ,^[4,5]

$$T_{\text{TF}}[\rho] = C_F \int d\mathbf{r} \rho^{5/3}(\mathbf{r}). \quad (1)$$

This expression was later complemented in 1935 by the addition of the von Weizsacker term,^[6]

$$T_{\text{W}}[\rho] = \frac{1}{8} \int d\mathbf{r} \frac{|\nabla \rho(\mathbf{r})|^2}{\rho(\mathbf{r})} \quad (2)$$

leading to the approximate expression:

$$T_s[\rho] \sim T_{\text{TF}}[\rho] + T_{\text{W}}[\rho]. \quad (3)$$

In the following decades, several attempts were made in order to develop perturbation series approximations for the kinetic energy functional. Expansions based on many-body perturbation theory, however, did not always prove practical because of the appearance of divergent terms in finite systems. Nevertheless, these expansions have been useful for slowly varying density regimes.^[7] In addition, using the semiclassical neutral atom

theory, modified fourth-order terms have been developed that show improvements over semilocal functionals.^[8] Many approaches have been tried on this problem and the list of approximate functionals has grown in size during the last decades.^[1,3,9–18] Moreover, there have been many attempts to obtain more accurate functionals by combining in a variety of ways T_{TF} and T_W . But the fact that no expression having the necessary accuracy has been derived so far over a period comprising almost 90 years truly attests to the difficulty of the problem at hand. Another recent approach relies in the determination of the Pauli potential via the solution of a differential equation.^[19] Let us also mention a proposal to evaluate the electronic kinetic energy density from the experimental (multipole-fitted) electron density.^[20]

From the perspective of information theory, $T_W[\rho]$ corresponds to the local component of the noninteracting kinetic energy. The remaining non-local part is associated with the Fisher information. Its nature is related to nonlocal contributions coming from the Fermi hole.^[21] This nonlocal part is also known as the Pauli kinetic energy term, $T_p[\rho]$ which is defined as

$$T_p[\rho] = T_s[\rho] - T_W[\rho] = \int d\mathbf{r} \rho^{5/3}(\mathbf{r}) F_p[\rho(\mathbf{r}); \mathbf{r}], \quad (4)$$

where $F_p[\rho(\mathbf{r}); \mathbf{r}]$ is the Pauli kinetic energy enhancement factor.

In the present work, we use the Liu-Parr power series expansion in order to represent directly the Pauli functional $T_p[\rho]$.^[22] This expansion belongs to the broader category of density functionals constructed from the moments of the electron density and is based on the fact that, due to the exponential decay of molecular electron densities, the multipole moments completely and uniquely determine the electron densities.^[23–31] This fact, in turn allows the representation of any density functional as a function of the moments of the system. Clearly, the present work has relevance for orbital-free methods and direct approximations to the one-particle density equation. In fact, as has been thoroughly discussed by Chakraborty et al.,^[32] there exists an intrinsic connection between the orbital-free method and the Euler-Lagrange equations for the density.

In particular, we explore the effects of varying the expansion length and of choosing different sets of atoms for the purpose of optimizing through a minimum-square fit the coefficients of this expansion. We compare an all-shell fit versus a shell-by-shell fit. We present a justification for the use of the Liu-Parr expansion to $T_p[\rho]$ by inspecting the behavior of this functional under coordinate scaling. We discuss the importance of including in the functionals, from the outset, characteristics related to shell structure and argue about the importance of a shell-by-shell coefficient optimization. In a previous work,^[33] the three-term Liu-Parr expansion was employed to represent the noninteracting kinetic energy functional $T_s[\rho]$. This representation was used, in turn, to assess the behavior of the Pauli enhancement factor.

The noninteracting kinetic energy represented by the Liu-Parr expansion is an example of an explicit functional of the one-particle density. However, this functional is not exact when the series is truncated. In addition, little is known about the convergence of these functional series. There exists, on the other hand, functionals which are, in principle, exact but which adopt an implicit dependence on the one-particle density. These functionals^[34] arise in the context of the local-scaling transformations version of density functional theory, LS-DFT. In particular, in this context the functional T_s , takes the form:

$$T_s[\rho] = T_W[\rho] + \frac{1}{2} \int d\mathbf{r} \rho^{5/3}(\mathbf{r}) A_N[\rho(\mathbf{r}); \mathbf{r}], \quad (5)$$

where $A_N[\rho(\mathbf{r}); \mathbf{r}]$ is an implicit functional of the one-particle density (see below). Note that the von Weizsacker term $T_W[\rho]$, which is an explicit functional of the one-particle density emerges in a natural fashion in this derivation. The term $A_N[\rho(\mathbf{r}); \mathbf{r}]$ which, except for a numerical factor is equivalent to the Pauli kinetic energy enhancement factor is, however, nonlocal and is closely related to the shell structure of the system. In the case of atoms, for example, A_N describes the hills and basins which lead to potentials that localize electrons in shells.

Several approximate realizations of the Pauli enhancement factor derived from the exact local-scaling expression have been studied by Ludeña et al.^[35] In particular, applications to first-row atoms and ions and to the diatomic molecules Na_2 and Al_2 ^[36] have shown that molecular kinetic energy enhancement factors may be accurately approximated by the addition of enhancement factors originally designed for atoms.

In section 2, we discuss the explicit representation of $T_p[\rho]$ given by the Liu-Parr expansion. In section 2.1, we present the results of applying the Liu-Parr representation of these functionals to atoms, from Li to Kr (including their positive and negative monoions) and explore both the effects that the size n of the expansion and a shell-by-shell mean-square optimization of the expansion coefficients have on the values of the noninteracting kinetic energy functional. In this section, we also discuss, for comparison purposes, the implicit functional form obtained through the application of local-scaling transformations. In section 4, we present some conclusions.

2 | REPRESENTATION OF THE PAULI TERM AS A FUNCTIONAL OF ρ

2.1 | The explicit functional representation for T_p in terms of the Liu-Parr expansion

We apply the Liu and Parr^[22] power series expansion originally used for the noninteracting kinetic energy functional T_s to represent, in the present case, the Pauli kinetic energy functional:

$$T_p[\rho] = \sum_{j=1}^n C_j \left[\int d\mathbf{r} \rho^{[1+2/3j]}(\mathbf{r}) \right]^j. \quad (6)$$

It follows from this expression that the Pauli enhancement factor is given by

$$F_p[\rho(\mathbf{r}); \mathbf{r}] = \sum_{j=1}^n C_j \rho^{(2/3)(1/j-1)}(\mathbf{r}) \left[\int d\mathbf{r} \rho^{[1+2/3j]}(\mathbf{r}) \right]^{j-1}. \quad (7)$$

The strict condition that the kinetic energy functional T_p must fulfill in order to be representable by Equation 6 is that it scales as

$$T_p^\lambda = \lambda^2 T_p \quad (8)$$

upon simple coordinate scaling, namely, $\mathbf{r} \rightarrow \mathbf{f} \equiv \lambda \mathbf{r}$ where λ is a constant. In order to prove this condition, let us first notice that

$$T_s^\lambda = \lambda^2 T_s \quad (9)$$

where

$$T_s[\rho] = \frac{1}{2} \sum_{i=1}^N \int d\mathbf{r} \nabla_{\mathbf{r}} \phi_i^{*\lambda}(\mathbf{r}) \nabla_{\mathbf{r}} \phi_i^\lambda(\mathbf{r}). \quad (10)$$

In addition, it can be easily shown that the von Weizsäcker term under coordinate transformation also goes into

$$T_W^\lambda = \lambda^2 T_W, \quad (11)$$

where

$$T_W^\lambda = \frac{1}{8} \int d\mathbf{r} \frac{|\nabla_{\mathbf{r}} \rho^\lambda(\mathbf{r})|^2}{\rho^\lambda(\mathbf{r})}. \quad (12)$$

Since $T_p = T_s - T_W$, it follows that also $T_p^\lambda = \lambda^2 T_p$.

A very simple use of the Liu-Parr expansion, where $T_s[\rho]$ is represented by its first term and the expansion coefficient is adjusted to the G1 set has been explored previously^[37]; it leads, however, to poor results. In the original three-term Liu-Parr expansion for $T_s[\rho]$ the coefficients were fixed by an optimal least-square fit to the “exact” Hartree-Fock values for atoms from H to Kr. The aptness of this expansion to represent the shell structure of atoms was examined recently.^[33] By and large, it reproduces quite closely the shape of the enhancement factor of the atoms considered, provided that a local contribution $v \nabla^2 \rho(\mathbf{f})$ (where v is a parameter) which does not contribute to the energy is added. This three-term expansion, however, does not lead to satisfactory values of the noninteracting kinetic energy $T_s[\rho]$ for the thirty six atoms examined going from H to Kr.^[33]

2.2 | The importance of introducing shell structure traits into approximations to T_p

The enhancement factor involves nonlocal effects which arise from the Pauli Exclusion Principle and which are responsible for the shell structure in atoms and molecules. Shell structure is an important ingredient in the description of electronic structure as it determines the periodicity of chemical properties of elements. In fact, periodicity arises from the formation of filled inner atomic shells and the presence of valence electrons characterizing the groups or families. The importance of employing shell-structure-inducing characteristics in the elaboration of approximate kinetic energy functionals for orbital-free molecular dynamics has been recently emphasized by Finzel.^[38–43]

In a remarkable paper of 1927, Pauling^[44] developed a view of many-electron atoms in terms of electrons which fill atomic shells according to the Pauli Exclusion Principle.^[45] This happened in an early period when quantum mechanics was just being developed and when, strictly speaking, only the hydrogen atom had been satisfactorily explained by Schrödinger.^[46] Pauling's idea was to assume the existence of electron shells in atoms, a supposition already adopted in the interpretation of X-ray spectra.^[47] These shells effectively shielded the nuclear charge and allowed the treatment of an individual electron placed outside these shells in a manner akin to that of an electron in a hydrogen-like atom subject to a screened nuclear potential. In fact, this idea was later carried over by Slater^[48] to the determination of atomic shielding constants.

However, although not based on a quantum mechanical justification, the concept of shell structure was amply used already in the systematization of atomic properties. As mentioned by Parr and Zhou,^[49] “For atoms, the shell structure was known even before the advent of quantum mechanics. The periodic table itself is nothing but a concise summary of experimental observation of atomic shell structures.”

The concept of atomic shells has been investigated through the analysis of one-electron radial densities in atoms, and of chemical indicators such as the curvature of the electron position uncertainty, described in terms of functions of the density.^[50] For a review of the connection of shell structure and chemical reactivity indicators, see Chattaraj and Maiti.^[51]

In some recent works, Finzel^[39–43] has examined how to incorporate the Pauli Exclusion Principle in the design of kinetic energy functionals for orbital-free treatments, through the concept of ideal atomic shells. This very simply idea captures, somehow, important characteristics that one should include in energy functionals expressed in terms of the one-particle density. One may conclude from these works that it is essential to

TABLE 1 Expansion coefficients $\{C_i\}_{i=1}^n$ of the Liu-Parr power series for T_p optimized for sets of atoms Li-Kr (All-shells), Li-Ne (L-shell), Na-Ar (M-shell), and K-Kr (N-shell)

<i>n</i>	All-shells	L-shell	M-shell	N-shell
3	0.50145548	−0.70827560	−0.49916121	0.77305110
	0.11749261	0.51142416	0.34150237	0.07679978
	−0.00178070	−0.02622196	−0.00969680	−0.00086940
4	−0.50351732	−1.34685487	−0.92354015	−0.78959189
	0.36610077	0.99982746	0.50180167	0.43176951
	−0.01406182	−0.10709152	−0.02313519	−0.01708877
5	0.00017203	0.00388677	0.00033782	0.00021186
	−0.40390064	1.66689817	−0.28082566	−1.17675483
	0.32963667	−1.92826229	0.12748911	0.54378736
6	−0.01094879	0.61521502	0.03095660	−0.02471010
	0.00007094	−0.06671487	−0.00268474	0.00041571
	0.00000113	0.00244766	0.00005871	−0.00000195
7	−0.26446661	14.72116773	−1.95907270	−0.98342596
	0.25727470	−16.38732425	1.75552566	0.45279987
	−0.00160415	5.13997716	−0.32626622	−0.01379253
8	−0.00043257	−0.71854176	0.02903249	−0.00014306
	0.00001330	0.04790267	−0.00120904	0.00001106
	−0.00000011	−0.00124368	0.00001908	−0.00000011
9	−0.97766639	17.68345611	−1.81305192	−1.69610763
	0.78400017	−19.25215980	0.52406583	1.23945355
	−0.09729093	5.74886960	0.16471148	−0.16932096
10	0.00703667	−0.72353729	−0.04358349	0.01198209
	−0.00027645	0.03570429	0.00399794	−0.00044592
	0.00000542	0.00015632	−0.00016451	0.00000828
11	−0.00000004	−0.00004839	0.00000256	−0.00000006

include from the outset these shell-determining traits into the energy functionals. This is the reason why we have set up a procedure for shell-by-shell optimization which we have applied to the calculation of the expansion coefficients.

3 | CALCULATION AND RESULTS

As described in Equation 6, we apply the Liu-Parr power series expansion to represent the Pauli kinetic energy functional. The first set of expansion coefficients is obtained, as in a previous work,^[33] by carrying out a least-square fit for the noninteracting kinetic energies over the whole set of atoms from Li to Kr. These coefficients are listed in the second column of Table 1, for the different selections of *n*, the series length, ranging from *n* = 3 to *n* = 7. The standard kinetic energy values are taken from the Clementi-Roetti tables.^[52] These optimized coefficients are denoted as the “All-shells” ones. However, in order to incorporate shell-structure traits, we carry out a shell-by-shell coefficient optimization for the Liu-Parr expansion. To this purpose, we consider three separate sets of atoms, each one of them corresponding to a given outer-atomic shell. Thus, the first set contains atoms from Li to Ne which have an outer L-shell. The second, atoms from Na to Ar (M-shell) and the third, atoms from K to Kr (N-shell). In this way, a particular set of optimized coefficients is obtained for each one of these sets of atoms which are denoted as the L-shell, M-shell, and N-shell, respectively. The set of atoms from Li to Kr formed by the union of the L-shell, M-shell, and N-shell atoms is called the “LMN-shells” set. In Table 1, we also present in columns 3, 4, and 5 the values of optimized coefficients corresponding to the L-shell, M-shell, and N-shell, respectively.

The assessment of the accuracy of the noninteracting kinetic energy functional has been traditionally made resorting to the percent error, Δ_p , defined by

TABLE 2 Mean absolute percent errors (MAPEs), Δ_{abs} , of the noninteracting kinetic energy, $T_s[\rho]$ for n -term expansions of $T_p[\rho]$ for the ground state of neutral atoms

n	$\Delta_{\text{abs}}^{\text{a}}$	$\Delta_{\text{abs}}^{\text{b}}$	$\Delta_{\text{abs}}^{\text{c}}$	$\Delta_{\text{abs}}^{\text{d}}$	$\Delta_{\text{abs}}^{\text{e}}$
3	2.9512	0.1549 (1.3804)	0.2527 (1.0204)	0.0271 (1.6411)	0.1682 (1.4245)
4	0.2839	0.0835 (0.2494)	0.2651 (0.0990)	0.0129 (0.2606)	0.0342 (0.3113)
5	0.2702	0.0373 (0.2125)	0.0817 (0.2077)	0.0104 (0.1065)	0.0296 (0.2618)
6	0.3244	0.0357 (0.1779)	0.0757 (0.2134)	0.0046 (0.0884)	0.0318 (0.2020)
7	0.1521	0.0147 (0.1342)	0.0290 (0.1040)	0.0020 (0.0953)	0.0140 (0.1648)

^aAll-shells.

^bLMN-shells (ABC-set).

^cL-shell (A-set).

^dM-shell (B-set).

^eN-shell (C-set).

$$\Delta_i = 100 |T_s^{\text{app}}(i) - T_s^{\text{HF}}(i)| / T_s^{\text{HF}}(i) \quad (13)$$

whose mean absolute percent error (MAPE) is

$$\Delta_{\text{abs}} = (1/N) \sum_{i=1}^N \Delta_i. \quad (14)$$

For example, in Ref. 53, the approximate kinetic energy functionals are ranked according to how small the MAPE value Δ_{abs} is.

However, this criterion may be misleading in cases where functionals leading to very small values of Δ_{abs} may nonetheless, still be far away from accurately approximating the Hartree-Fock or the Kohn-Sham values of $T_s[\rho]$, (see below for a discussion on this point). For this reason, we also make use of the following parameters which directly measure the proximity of trial functionals to the reference ones. These are the noninteracting kinetic energy absolute error:

$$\Delta T_i = |T_s^{\text{app}}(i) - T_s^{\text{HF}}(i)| \quad (15)$$

and the mean absolute error (MAE) given by

$$\Delta T_{\text{abs}} = (1/N) \sum_{i=1}^N \Delta T_i. \quad (16)$$

These parameters are measured in kcal/mol.

3.1 | Neutral atoms

We present the results of the calculations for T_p for neutral atoms obtained through the application of Equation 6. In Figure 1A, the values from Li to Kr of Δ_i described in Equation 13 and computed for $n = 4$ and $n = 5$ are graphed as functions of the atomic number. These values correspond to the “LMN-shells” set. For completeness, we have also graphed the values corresponding to the “All-shells” set. In Figure 1B, we present the same graphs as in Figure 1A but for $n = 6$ and $n = 7$. Because the values of Δ_i become increasingly small as the atomic number increases, we snip the graphs in order to highlight this effect. The values of the MAPE Δ_{abs} for each one of the Liu-Parr expansions for n ranging from 3 to 7 are presented in Table 2. In column 2, we list the Δ_{abs} values obtained from the coefficients optimized using an “All-shells” approach for atoms from Li to Kr. In column 3, by contrast, we present the values obtained by means of a shell-by-shell optimization (LMN-shells). It is interesting to notice that the “LMN-shells” values for Δ_i are about an order of magnitude smaller than the “All-shell” ones. This shows quite clearly that the inclusion of shell-structure traits is fundamental for a good representation of the power series expansion. In columns 4, 5, and 6 of Table 2, the Δ_{abs} values for the sets characterized as L-shell (Li-Ne), M-shell (Na-Ar), and N-shell (K-Kr) are listed. Of particular interest is the fact that these values for the M-shell for expansions with $n = 6$ and $n = 7$ are an order of magnitude smaller than those of the L-shell and N-shell.

We have also examined the accuracy of these functionals by further studying the behavior of the absolute error ΔT_i , Equation 15, measured in kcal/mol. Certainly, if one wishes to ascertain how close an energy value is to the true experimental one, one must use a property measured in kcal/mol, as chemical accuracy is customarily assigned the value of 1 kcal/mol. These values are graphed in Figure 2A for $n = 4$ and $n = 5$ and in Figure 2B, for $n = 6$ and $n = 7$, respectively. It is seen from these figures that the “All-shell” fit presents a saw-edge structure which lies above those of the “LMN-shells,” for all cases considered.

The MAEs ΔT_{abs} corresponding to these graphs are presented in Table 3. In column 2 of this table, we have listed the ΔT_{abs} for Liu-Parr expansions going from $n = 3$ to $n = 7$ whose coefficients have been optimized by an “All-shell” procedure. The values listed in column 3 have been

TABLE 3 Mean absolute errors (MAEs), ΔT_{abs} , in kcal/mol of the noninteracting kinetic energy, $T_s[\rho]$ for n -term expansions of $T_p[\rho]$ for the ground state of neutral atoms

n	ΔT_{abs}^a	ΔT_{abs}^b	ΔT_{abs}^c	ΔT_{abs}^d	ΔT_{abs}^e
3	2225.5	652.7 (1326.7)	63.8 (244.0)	50.8 (887.2)	1182.0 (2003.2)
4	343.1	168.5 (307.6)	42.3 (176.9)	24.2 (158.2)	288.7 (432.0)
5	329.3	131.4 (251.7)	15.4 (73.6)	18.4 (37.9)	233.2 (426.0)
6	327.0	130.5 (235.4)	8.0 (64.0)	7.7 (31.0)	239.5 (402.5)
7	187.0	52.8 (98.0)	2.9 (7.9)	4.1 (29.3)	96.6 (168.7)

^aAll-shells.^bLMN-shells (ABC-set).^cL-shell (A-set).^dM-shell (B-set).^eN-shell (C-set).

calculated adjusting to coefficients to the “LMN-shells” set. It is clear from these results that the shell-by-shell approach yields a much better approximation than the all-shell one. Moreover, when one decomposes the total values into their L-shell, M-shell, and N-shell contributions (listed in columns 4–6, respectively) it is clearly seen that the approximate noninteracting kinetic energy values are quite close to the Clementi-Roetti ones for the L-shell and M-shell. In fact, for expansion lengths $n = 6$ and $n = 7$, the deviation amounts just to a few kcal/mol. This result quite clearly indicates that the kinetic energy functional is approaching chemical accuracy in these cases.

Let us compare now the behavior of the kinetic energy functionals given by the different approximations considered in this work and graphed in Figures 1 and 2. First, from the behavior of the percent errors depicted by the blue and red lines in Figure 1A corresponding to the LMN-shells optimization of the coefficients for $n = 4$ and $n = 5$, respectively, it is seen that both functionals present considerable deviations for almost all the first-row atoms. However, from Na to Ar, they evince a highly improved behavior. There is some discrepancy for K, Ca, and the transition metals from Sc to Cr. For the remaining third-row atoms, although the approximation improves, the curve, however, has a zig-zag shape. A similar behavior is observed in Figure 1B. One can see, nevertheless, that the fit from B to Ar is quite good.

When we take a look at the behavior of these approximate functionals in Figure 2, we see that the absolute errors ΔT_i from Li to Ar are very small both in Figure 2A,B. In fact, the accuracy of the approximations for $n = 6$ and $n = 7$ is quite impressive. This result can be further corroborated when we consider the values of the MAEs ΔT_{abs} . These errors (in kcal/mol) are 187.0, 52.8, 2.9, 4.1, and 96.6 for the All-shell, LMN-shell, L-shell, M-shell, and N-shell sets, respectively. Moreover, the MAE values of 2.9 and 4.1 corresponding to $n = 7$ for the L-shell and M-shell are very close to those required for attaining chemical accuracy. On the other hand, the absolute error for the N-shell set (96.6 kcal/mol) is still outside the range of chemical accuracy.

The present discussion also clarifies the claim that an examination of the absolute errors ΔT_i values is necessary as the MAEs Δ_{abs} by themselves do not suffice to discriminate among functionals. For example, from Table 2 we have for $n = 7$ the following MAPE values: 0.1521, 0.0147, 0.0290, 0.0020, and 0.0140 corresponding to the All-shell, LMN-shell, L-shell, M-shell, and N-shell sets, respectively. Although, for example, those of the LMN-shell, M-shell, and N-shell sets are in the same range, their corresponding absolute errors are quite different. This is the reason why we have resorted to ΔT_{abs} as an auxiliary indicator.

In order to rule out the possibility that the effects which we ascribe to shell structure arise instead from the increased number of expansion coefficients characterizing the shell-by-shell approach, we have carried out calculations using selected sets of atoms, which we denote by A, B, and C where the atoms sample simultaneously the three different shells. Each one of these sets contains the following neutral atoms (labeled by their atomic numbers):

$$A = \{4, 5, 12, 13, 20, 21, 22, 23\}, \quad (17)$$

$$B = \{6, 7, 14, 15, 24, 25, 32, 33\}, \quad (18)$$

$$C = \{8, 9, 10, 11, 16, 17, 18, 19, 26, 27, 28, 29, 30, 31, 34, 35, 36, 37\}. \quad (19)$$

Note that the number of atoms in each one of the sets A, B, and C is the same as in the L-shell, M-shell, and N-shell sets, respectively. Following the same procedure as above, the optimal least-square coefficients are calculated for each one of these sets, for different expansion lengths $n = 3, \dots, 7$. The results of these calculations are included in parentheses in Tables 2 and 3. Considering that in both tables, the values corresponding to the ABC-set, A-set, B-set, and C-set are considerably larger than those obtained for the LMN-shell, L-shell, M-shell, and N-shell sets, we may safely conclude that the shell-by-shell results do not emerge from a spurious size effect but rather reflect properties arising from shell structure.

An important issue concerning these functionals is whether the best expansions for shell-adapted functionals are able to reproduce closely the exact enhancement factor given by Equation 7 without having to resort to the addition of a Laplacian term.^[33] This issue has been recently

TABLE 4 Comparison with mean absolute percent errors (MAPEs), Δ_{abs} , of the noninteracting kinetic energy, $T_s[\rho]$ for neutral atoms

Functional	Variables	Δ_{abs}
Liu-Parr (this work) $n=7$ M-shell	ρ	0.0020
Liu-Parr (this work) $n=7$ N-shell	ρ	0.0140
Liu-Parr (this work) $n=7$ LMN-shell	ρ	0.0147
Liu-Parr (this work) $n=7$ L-shell	ρ	0.0290
Tran-Wesołowski	$\rho, \nabla \rho$	0.0804 ^a
Conjoint-Fuentealba	ρ	0.0992 ^a
Haq et al.	$\rho, \Delta \rho$	0.1023 ^a
Lee, Lee, and Parr	$\rho, \nabla \rho$	0.1039 ^a
Fuentealba, Reyes	$\rho, \nabla \rho$	0.1184 ^a
Lembarki and Chermette	$\rho, \nabla \rho$	0.1400 ^a
Liu-Parr (this work) $n=7$ All-shell	ρ	0.1521
Conjoint PW81	$\rho, \nabla \rho$	0.1630 ^a

^aFrom Table 3 of Ref. 53.

examined by Ludeña et al.,^[54] In the present work, we further examine it by plotting in Figure 3 the enhancement factors of the functionals corresponding to $n=7$ expansions both in the All-shell and shell-by-shell approximations. Aluminum atom is chosen as a representative member of the M-shell set containing only s and p electrons. It is clearly seen that these expansions are not sufficient to reproduce the behavior of the exact enhancement factor (calculated at the Hartree-Fock level) as they show spurious negative regions at large r (explicitly highlighted in the inset of Figure 3). This behavior does not comply with the requirement of strict positivity of this factor. It is seen in Figure 3 that a closer fit is provided by the shell-by-shell optimized functional. In addition, the exact asymptotic behavior at the nucleus^[55,56] is not fulfilled either by these expansions which show a slight negative deviation at the nucleus.

It is instructive, at this point, to recall the work of Chan and Handy^[57] who performed an extensive study on the least-square fitting of the non-interacting kinetic energy functional. In their work, they consider the variational functional

$$F[\rho] = \int d^3\mathbf{r}_1 \cdots \int d^3\mathbf{r}_m f[v_1(\mathbf{r}_1), v_2(\mathbf{r}_1), \dots], \quad (20)$$

where the density variables are $v_i(\mathbf{r}) \in \{\rho, x, y, \tau\}$, with $x = |\nabla \rho|/\rho^{4/3}$, $y = \nabla^2 \rho/\rho^{5/3}$ and $\tau = \sum_{i=1}^N |\nabla \phi_i|^2/\rho^{5/3}$. The functional basis $\{\mu_i(v_1, v_2, \dots)\}$ is then constructed from the density variables. The kernel f of Equation 20 is a function of an arbitrary finite number of density variables and can then be expanded as

$$f = \sum_i c_i \mu_i(v_1, v_2, \dots). \quad (21)$$

The ΔT_{abs} values obtained by this fitting method employing both analytical basis sets as well as finite-element basis sets may be estimated (from Figure 8 of Ref. 57) to be 58 mH or 36.4 kcal/mol for an expansion length of $n=24$.

TABLE 5 Mean absolute percent errors (MAPEs), Δ_{abs} of noninteracting kinetic energy, $T_s[\rho]$ for n -term expansions of $T_p[\rho]$ of positive ions from Be^+ to Kr^+

n	$\Delta_{\text{abs}}^{\text{a}}$	$\Delta_{\text{abs}}^{\text{b}}$	$\Delta_{\text{abs}}^{\text{c}}$	$\Delta_{\text{abs}}^{\text{d}}$	$\Delta_{\text{abs}}^{\text{e}}$
3	2.5430	0.2779	0.6531	0.0595	0.2042
4	0.5114	0.2261	0.5905	0.1215	0.1039
5	0.3801	0.4630	1.5247	0.0826	0.1425
6	0.4201	1.4504	5.5102	0.1820	0.1368
7	0.2941	1.6753	6.4893	0.2646	0.0737

^aAll-shells.

^bLMN-shells.

^cL-shell.

^dM-shell.

^eN-shell.

In order to compare Chan and Handy's result with our present ones, let us recall, that for each shell, the expansion length takes at most the value of $n = 7$. Nonetheless, we can see from Table 3 that the ΔT_{abs} values corresponding to the L-shell and M-shell sets are considerably lower already for $n = 5$ and attain values approaching chemical accuracy for $n = 6$ and $n = 7$. These results seem to indicate that a brute force approach to coefficient fitting yields errors which are much higher than those in which shell-sustaining traits are introduced from the outset.

To end this subsection, we compare in Table 4 the results of the present work with those presented by Tran and Wesolowski.^[53] Let us indicate, however, that the sets from which these results are obtained are different. For example, for the result quoted as "Liu-Parr (this work) $n = 7$ M-shell" the set is formed by the eight atoms in the M-shell. By contrast, "Liu-Parr (this work) $n = 7$ LMN-shell" is obtained from the set of 34 atoms from Li to Kr. The set used for the Tran-Wesolowski results are obtained from the fitting set formed by He, Be, Ne, Mg, Ar, Ca, Zn, Sr, Pd, Cd, and Xe. Thus, if not entirely adequate, the comparison made in Table 4 at least shows the tendencies in MAPE values arising from the introduction of shell-constraining conditions in the functionals.

3.2 | Positive and negative ions

We have also applied the Liu-Parr expansion to compute the noninteracting kinetic energy for monpositive and mononegative ions corresponding to atoms from Li to Kr. We have used in these applications the same expansion coefficients obtained for the neutral atoms, in their "All-shell" and "LMN-shell" realizations. The idea behind this application is to determine how well the kinetic energy functional for neutral atoms also behaves in those cases in which an atom either loses or gains an electron, that is, how it fares in situations resembling chemical reactions in which the charges of atoms change.

The results for the ΔT_i values for positive ions are presented in Figure 4A and those for negative ions in Figure 4B. In addition, in Tables 5 and 6 we present the Δ_{abs} values and, in Tables 7 and 8, the ΔT_{abs} values for positive and negative ions, respectively.

It is seen from Figure 4A that the best fit for the kinetic energies of positive ions from Be^+ to Kr^+ corresponds to the "All-shell" coefficient set. In fact, the "LMN-shell" coefficients lead to poor approximations, particularly for the "L-shell." Also, from Figure 4 we can infer that for the "M-shell" and "N-shell" the discrepancies with respect to the exact values are quite significant. Seemingly, the shell-by-shell optimization, which led to important improvements for neutral atoms, does not work in the present case. In fact, there is almost no difference between a shell-by-shell and an all-shell situation.

The results for the total noninteracting kinetic energies of neutral and positive ions could be used to estimate ionization energies. The ionization energy is defined as the difference between total energies of ionized and neutral atom,

$$\text{IE}^{\text{HF}}(A) = E_{\text{tot}}^{\text{HF}}(A^{+1}) - E_{\text{tot}}^{\text{HF}}(A), \quad (22)$$

which in the Hartree-Fock case reduces to the noninteracting kinetic energy difference

$$\text{IE}^{\text{HF}}(A) = -T_s^{\text{HF}}(A^{+1}) - T_s^{\text{HF}}(A) \quad (23)$$

due to the fact that the virial relation, $T_s = -E_{\text{tot}}$, is satisfied. Approximate non-self-consistent total energy (hence the approximate ionization energy) could be calculated with use of the Hartree-Fock densities (and orbitals for the exchange term) with replacement of the Hartree-Fock kinetic energy, T_s^{HF} , by an approximate orbital-free term, T_s^{app} , in the HF total energy $E_{\text{tot}}^{\text{HF}} = T_s^{\text{HF}} + V^{\text{HF}}$, where $V^{\text{HF}} = E_{\text{Ne}}^{\text{HF}} + E_{\text{H}}^{\text{HF}} + E_{\text{x}}^{\text{HF}}$ is the sum of usual nuclear-electron, Hartree and exchange terms. This is similar to the method used in Ref. 58 to calculate non-self-consistent orbital-free total energies. Thus, one obtains $E_{\text{tot}}^{\text{app}} = T_s^{\text{app}} + V^{\text{HF}}$, and the approximate ionization is equal to

$$\begin{aligned} \text{IE}^{\text{app}}(A) &= (T_s^{\text{app}}(A^{+1}) + V^{\text{HF}}(A^{+1})) - (T_s^{\text{app}}(A) + V^{\text{HF}}(A)) \\ &= (T_s^{\text{app}}(A^{+1}) - T_s^{\text{app}}(A)) - 2(T_s^{\text{HF}}(A^{+1}) - T_s^{\text{HF}}(A)). \end{aligned} \quad (24)$$

where the last equality follows from Equations 22 and 23. Approximate ionization energies of atoms were calculated with use of Equation 24 for the Thomas-Fermi (TF) and the Liu-Parr power series (with $n = 3$) orbital-free functionals. The Liu-Parr power series expansion ($n = 3$) provides better results for ionization energies as compared to the TF values only in few cases.

For example in case of the N atom, $\text{IE}^{\text{HF}} = 0.513$, $\text{IE}^{\text{TF}} = 0.758$, and $\text{IE}^{\text{LP}^3} = 0.518$. For C, $\text{IE}^{\text{HF}} = 0.396$, $\text{IE}^{\text{TF}} = 0.595$, and $\text{IE}^{\text{LP}^3} = 0.411$. For S, $\text{IE}^{\text{HF}} = 0.333$, $\text{IE}^{\text{TF}} = 0.440$, and $\text{IE}^{\text{LP}^3} = 0.347$. Overall, the ionization energy errors of approximate functionals are relatively large and must be related to relatively large errors in kinetic energies of positive ions reported in Table 7. Of course, it must be emphasized that we have carried over the coefficients optimized for neutral atoms to the case of positive and negative ions. The ΔT_{abs} 's presented in Table 7 for positive ions have values of around 600 kcal/mol for the best fits attained with all-shell coefficients.

The same behavior is also seen in the case of the negative ions from Li^- to Br^- , where, again, the "L-shell" coefficients of the neutral atoms lead to substantial errors. For negative ions, we observe from Table 8 that the closest absolute error is of the order of 400 kcal/mol. These results compare satisfactorily, though, with those obtained previously^[33] for the Liu-Parr expansion with $n = 3$.

TABLE 6 Mean absolute percent errors (MAPEs), Δ_{abs} of noninteracting kinetic energy, $T_s[\rho]$ for n -term expansions of $T_p[\rho]$ for negative ions from Li^- to Br^-

n	$\Delta_{\text{abs}}^{\text{a}}$	$\Delta_{\text{abs}}^{\text{b}}$	$\Delta_{\text{abs}}^{\text{c}}$	$\Delta_{\text{abs}}^{\text{d}}$	$\Delta_{\text{abs}}^{\text{e}}$
3	2.9260	0.2728	0.7836	0.1075	0.1348
4	0.2082	0.1464	0.2361	0.1897	0.0932
5	0.2447	0.4944	1.7493	0.1921	0.1135
6	0.3399	1.6850	7.0970	0.1999	0.1142
7	0.1870	1.9618	8.4670	0.1937	0.0670

^aAll-shells.

^bLMN-shells.

^cL-shell.

^dM-shell.

^eN-shell.

3.3 | Comparison with an implicit functional $T_p[\rho]$ obtained by means of local-scaling transformations

Following López-Boada and Ludeña,^[34] let us consider the most general form of the kinetic energy functional expressed in terms of the first-order reduced density matrix, D_{Ψ}^1 coming from the N -particle wave function Ψ :

$$T[D_{\Psi}^1] = \frac{1}{2} \int d\mathbf{r}_1 \nabla_{\mathbf{r}_1} \nabla_{\mathbf{r}_1} D_{\Psi}^1(\mathbf{r}_1, s_1; \mathbf{r}_1', s_1')|_{\mathbf{r}_1'=\mathbf{r}_1, s_1'=s_1}. \quad (25)$$

The spin-dependent 1-matrix corresponding to a noninteracting system described by a single Slater determinant is defined by

$$D_{\Psi}^1(\mathbf{r}_1, s_1; \mathbf{r}_2, s_2) = \sum_{i=1}^N \phi_{p,i}(\mathbf{r}_1) \sigma_{m_{s_1}}(s_1) \phi_{p,i}(\mathbf{r}_2) \sigma_{m_{s_2}}(s_2), \quad (26)$$

where the orthonormal single-particle set $\{\phi_{p,i}(\mathbf{r})\}_{i=1}^N$ is formed by locally scaled orbitals. These density-dependent orbitals are obtained through the application of local-scaling transformations to the orthonormal set $\{\phi_i(\mathbf{r})\}_{i=1}^N$:

$$\phi_{p,i}(\mathbf{r}) = \left[\frac{\rho(\mathbf{r})}{\rho_{\phi}(\mathbf{f}(\mathbf{r}))} \right]^{1/2} \phi_i(\mathbf{f}(\mathbf{r})), \quad (27)$$

where $\rho_{\phi}(\mathbf{r}) = \sum_{i=1}^N |\phi_i(\mathbf{r})|^2$.

For atoms, we can separate the radial and angular parts so that the locally scaled atomic orbital is given by

$$\phi_{p,i}(\mathbf{r}) = \sqrt{\frac{\rho(r)}{\rho_{\phi}(f)}} R_{n_l, l_l}(f) Y_{l_l, m_{l_l}}(\theta, \phi), \quad (28)$$

where we have assumed that the local-scaling transformation only affects the radial function. Substituting Equations 28 and 26 into Equation 25, and integrating over the angular coordinates we arrive, after some straightforward algebra, to the following expression for the kinetic energy functional:

TABLE 7 Mean absolute errors (MAEs), ΔT_{abs} in kcal/mol of noninteracting kinetic energy, $T_s[\rho]$ for n -term expansions of $T_p[\rho]$ for positive ions from Be^+ to Kr^+

n	$\Delta T_{\text{abs}}^{\text{a}}$	$\Delta T_{\text{abs}}^{\text{b}}$	$\Delta T_{\text{abs}}^{\text{c}}$	$\Delta T_{\text{abs}}^{\text{d}}$	$\Delta T_{\text{abs}}^{\text{e}}$
3	2528.5	949.4	267.7	140.9	1650.6
4	625.6	606.9	169.3	301.1	956.8
5	600.6	836.4	574.6	216.7	1251.3
6	601.8	1236.1	2166.8	375.9	1202.9
7	528.7	1137.4	2557.1	580.8	731.2

^aAll-shells.

^bLMN-shells.

^cL-shell.

^dM-shell.

^eN-shell.

TABLE 8 Mean absolute errors (MAEs), ΔT_{abs} in kcal/mol of noninteracting kinetic energy, $T_s[\rho]$ for n -term expansions of $T_p[\rho]$ for negative ions from Li^- to Br^-

n	$\Delta T_{\text{abs}}^{\text{a}}$	$\Delta T_{\text{abs}}^{\text{b}}$	$\Delta T_{\text{abs}}^{\text{c}}$	$\Delta T_{\text{abs}}^{\text{d}}$	$\Delta T_{\text{abs}}^{\text{e}}$
3	2089.2	567.3	162.5	231.7	863.5
4	408.9	458.2	59.7	379.9	648.9
5	396.1	611.3	406.9	387.2	782.8
6	410.8	894.8	1727.3	331.8	787.0
7	362.0	856.4	2054.3	396.3	561.3

^aAll-shells.^bLMN-shells.^cL-shell.^dM-shell.^eN-shell.

$$T_s[\rho] = T_W[\rho] + T_p[\rho; \lambda], \quad (29)$$

where $T_p[\rho; \lambda]$ is the implicit form of the Pauli potential:

$$T_p[\rho; \lambda] = \int_0^\infty dr r^2 \rho^{5/3}(r) [(1 + \mathbf{r} \cdot \nabla \ln \lambda(r))^{4/3} \tau_N + (1 + \mathbf{r} \cdot \nabla \ln \lambda(r)) - 2/3 \kappa_N]. \quad (30)$$

Here, τ_N and κ_N are radial and the angular kinetic energy modulating factors defined by

$$\tau_N = \frac{1}{\rho_\phi^{8/3}(f)} \frac{1}{2} \sum_{i=1}^{N-1} \sum_{j=i+1}^N \left[R_{n_i l_i}(f) \frac{dR_{n_j l_j}(f)}{df} - R_{n_j l_j}(f) \frac{dR_{n_i l_i}(f)}{df} \right]^2, \quad (31)$$

and

$$\kappa_N = \frac{1}{\rho_\phi^{5/3}(f)} \sum_{i=1}^N \frac{l_i(l_i+1)}{2} \left(\frac{R_{n_i l_i}(f)}{f} \right)^2, \quad (32)$$

where $f(r)$ satisfies the following first-order differential equation:

$$\frac{df(r)}{dr} = \frac{r^2}{f^2(r)} \frac{\rho(r)}{\rho_\phi(f)} \quad (33)$$

and where $\lambda(r) = f(r)/r$. It is clear that $f(r)$ and $\lambda(r)$ depend implicitly on $\rho(r)$, namely, $f(r) \equiv f([\rho(r)], r)$ and $\lambda(r) \equiv \lambda([\rho(r)], r)$.

In a previous work,^[34] we have used simple approximations for the radial orbital set $\{R_{n_i l_i}(r)\}$ given in terms of, for example, the set of Generalized Slater-Type Orbitals, GSTOs, defined by

$$R_{n_i l_i}(r) = P_{n_i l_i}(r) e^{-\alpha_{n_i l_i} r^\beta}, \quad (34)$$

where the $P_{n_i l_i}(r)$ are orthogonal polynomials satisfying the condition:

$$\int_0^\infty dr r^2 P_{n_i l_i}(r) e^{-\alpha_{n_i l_i} r^\beta} P_{n_j l_j}(r) e^{-\alpha_{n_j l_j} r^\beta} = \delta_{n_i n_j}. \quad (35)$$

The advantage of this representation is that each electron is described by a single GSTO. For the sake of comparing results for this approximation (an implicit functional of the one-electron density) with those of explicit functionals discussed below, we present in Figure 5 the absolute relative errors, Δ_i of Equation 13, associated with this functional, for atom spanning from Li to Ar.

But more generally, the local-scaling transformation expression for the kinetic energy functional $T_s[\rho]$ may be given in terms of arbitrary orthogonal polynomials. There exists a deep relationship between the orthogonality of polynomials and the appearance of shell structure. This point is elaborated extensively elsewhere.^[54]

We want to point out, however, that in the general formulation given by Equation 30, the particular form adopted by the enhancement factor through Equations 31 and 32 already endows the implicit functional with shell-structure-inducing characteristics. This observation contributes to justify the need for including from the outset these characteristics into approximate kinetic energy functionals designed for orbital-free molecular dynamics.

At this point, we would like to compare the results obtained for the noninteracting kinetic energy using the implicit functional generated through local-scaling transformations. We present in Figure 5 in addition to the Δ_i values corresponding the LS-functional, the results obtained using

FIGURE 1 Percent errors, Δ_i , of Equation 13 for neutral atoms from Li to Kr. A, For coefficients fitted to the “All-shells” set, these values are given in black for $n = 4$, and in green for $n = 5$; for those fitted to the “LMN-shells” set, they are given in red for $n = 4$, and in blue for $n = 5$. B, Same as in (A) but for $n = 6$, and $n = 7$. In order to enhance the view of small Δ_i values, the graphs are snipped to show two scales

the Liu-Parr expansion evaluated for the LMN-shells. The latter correspond to expansions with $n = 6$ and $n = 7$. In order to be able to compare the behavior of these approximations, we have used a snipped graph. As seen in Figure 5 that the Δ_i values of the LS-approximation deviate more pronouncedly from the reference ones of Clementi-Roetti as a function of increasing atomic number, than the values obtained from the Liu-Parr expansion.

4 | DISCUSSION

The problem of how to represent the noninteractive kinetic energy as a functional of the one-electron density still remains unsolved even though almost 90 years have elapsed since its original formulation. Its inherent difficulty stems from the fact that the kinetic energy, according to the virial theorem, has the same absolute magnitude as that of the total energy of a system. Thus, in order to attain chemical accuracy one must design functionals for $T_s[\rho]$ which differ from the exact one only by a few kcal/mol. All of the approximate functionals for the noninteracting kinetic energy that have been designed until now are still far from meeting this criterion. In the present work, however, we present some promising results which show that approximate expressions for the noninteracting kinetic energy can attain a precision closely approaching that of chemical accuracy. The approximate functional based on the Liu-Parr power series expansion has been constructed so as to incorporate from the outset shell-inducing traits. This was carried out by means of a shell-by-shell optimization of the expansion coefficients. The results show that for the first time an approximate functional can be built which has (for $n = 7$) a MAE value of 52.8 kcal/mol for the ground states of neutral atoms from Li to Kr, of 2.9 kcal/mol from Li to Ne (L-shell), 4.1 kcal/mol from Na to Ar (M-shell), and 96.6 kcal/mol from K to Kr (N-shell). Clearly, for the L-shell and M-shell these values show that the functional is approaching chemical accuracy. The issue of whether these values arise from an spurious effect due to increasing expansion

FIGURE 2 Absolute errors, ΔT_i , in kcal/mol, Equation 15 for neutral atoms from Li to Kr. A, For coefficients fitted to the “All-shells” set, the absolute errors are given in black for $n=4$, and in green for $n=5$; for those fitted to the “LMN-shells” set, they are given in red for $n=4$, and in blue for $n=5$. B, Same as in (A) but for $n=6$, and $n=7$

lengths of the Liu-Parr series was dealt with by performing calculations using sets that contain the same number of atoms as the L-shell, M-shell, and N-shell sets, but where the atoms involved sampled all shells. The results of these calculations clearly show the importance of incorporating shell-traits in the density power series expansions. Moreover, the present results yield much more accurate values than those obtained by an

FIGURE 3 Comparison of the behavior of the exact enhancement factor $F_p[\{R_i^{\text{HF}}\}]$ for the Al atom with the approximations given by the Liu-Parr expansions for $n=7$ with All-Shell and shell-by-shell optimized coefficients. The inset graph shows in detail the behavior of these approximate enhancement factors for negative values

FIGURE 4 Absolute errors, ΔT_i , in kcal/mol, Equation 15. A, Positive ions from Be^+ to Kr^+ with coefficients fitted to the “All-shells” set, in black for $n = 6$, and in green for $n = 7$; for those fitted to the “LMN-shells” set, in red for $n = 6$ and in blue for $n = 7$. B, Negative ions from Li^- to Br^- ; same labeling as in (A)

extensive least-square fitting such as that of Chan and Handy. We would like to emphasize, however, the fact that in addition to yielding accurate kinetic energy values, the functionals must be able to produce adequate potentials in the associated Euler-Lagrange equation allowing the calculation of accurate densities. This problem is, of course, related to the convexity conditions on the kinetic energy functional.

FIGURE 5 Values of the percent errors, Δ_i , from Li to Ar corresponding to the implicit local-scaling functional given by Equation 13 (solid red) evaluated using GSTOs. For comparison, the values of the explicit Liu-Parr functional (see below) are also presented for $n = 6$ (solid green) and $n = 7$ (solid blue) where the expansion coefficients have been obtained through a shell-by-shell optimization (LMN-shell set)

For positive and negative ions the results, however, are still far from being satisfactory. In conclusion, the results for neutral atoms (provided the shell-traits are incorporated) show that the present approach holds some promise.

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