The asymptotic expansion for $E$ is in powers of $Z^{-1/3}$, so if $I$ remains finite as $Z \to \infty$, the neutral and ion energies must agree for the first seven powers in such an expansion, a truly remarkable balancing act between quantum effects, the Pauli principle, and the Coulomb forces of nuclear attraction and interelectron repulsion. That $I$ remains bounded has been proven within Hartree–Fock.18 In this paper, we demonstrate by both calculation and analysis that (i) $I$ has no single limit as $Z \to \infty$, but remains column dependent; (ii) each column has a finite limit; (iii) the local (spin) density approximation (LSD10) of KS theory becomes very accurate (if not exact) for $I$ for certain cases; (iv) ETF theory becomes very accurate (if not exact) for the average of $I$ over an entire shell; (v) the shell-averaged difference in density between the neutral and its ion approaches that of TF.

Our most important results are shown in Fig. 1. We plot $I$ from various calculations, extrapolated to infinite row number, versus the column number for main-group elements ($s$ and $p$ valence shells). We calculate exchange exactly,19,20 using the optimized effective potential (OEP, which here should be indistinguishable from Hartree–Fock21), extrapolating all values to $Z \to \infty$. At the exchange level, LSD and PBE are almost exact for $p$-valence elements, and are highly accurate but inexact for the $s$-valence cases. Furthermore, ETF yields14 a single number (3.15 eV), very close to the $s$- and $p$-valence average (3.02 eV). When correlation is included, gradient effects are slight, and it is in the regime of large electron number that approximate density functionals work best, sometimes exactly.13,15,22 We speculate that LSDX on accurate densities becomes almost exact in this limit for $p$-shell cases, that ETF is exact for some shell-average, and that our XC results are extremely accurate and practically impossible to calculate with any other method.

To understand why local functionals become accurate in this limit, begin with total energies of neutral atoms, whose large-$Z$ expansion is

$$E_0(Z) = -c_q^{(0)} Z^{7/3} + 0.5 Z^2 - c_q^{(2)} Z^{5/3} + \cdots,$$

(1)

where $E_0(Z)$ is the energy of an atom with atomic number $Z$ and charge $Q$, and the $c_q^{(j)}$ are coefficients depending on the degree of ionization, $q = Q/Z$. We use atomic units

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A central problem of electronic structure is the calculation of the ground-state energy of the electrons of any atom, molecule, or solid, within the nonrelativistic Born–Oppenheimer limit. Density functional theory (DFT) is a popular choice, balancing computational efficiency with useful accuracy. The original DFT was that of Thomas1 and Fermi,2 TF theory, in which a local density approximation is made for the kinetic energy and the electron–electron repulsion is approximated by the simple Coulomb energy of the charge density. In the 1970s, Lieb and co-workers3 showed that the TF energy becomes relatively exact for neutral matter as $Z \to \infty$ in a specific way. The energy, $E$, grows in magnitude as $Z^{7/3}$, where $Z$ is the total charge. For atoms and their ions, the leading corrections in powers of $Z^{-1/3}$ were found by Scott,4 Dirac,5 Schwinger and others,6,7 as summarized by Englert.8 These corrections are given exactly by extended Thomas–Fermi (ETF) theory,10 which includes both the gradient correction for the kinetic energy (one-ninth the von Weizsacker functional), and the local density approximation for exchange (LSDX10).

However, TF theory and its extensions are insufficiently accurate to predict chemical properties.11 Modern DFT uses the Kohn–Sham (KS) scheme, in which only a very small fraction of the total energy, the exchange-correlation (XC), need be approximated. But the idea of asymptotic correctness was recently extended to KS, relating the success of KS theory becomes very accurate (if not exact) for $I$ for certain cases; (iv) ETF theory becomes very accurate (if not exact) for the average of $I$ over an entire shell; (v) the shell-averaged difference in density between the neutral and its ion approaches that of TF.

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TF energy is the smooth envelope of oscillation with $Q$, system, but the TF energy behaves as curves using a parabolic fit in $Z$ change. These were done using the Engel code, but with XC functional approximations, as well as the exact OEP for atoms and ions up to 2938 electrons using LSD and PBE the KS orbitals. We perform KS self-consistent calculations, kinetic energy is not approximated, but is found exactly from classical analysis. The TF energy is exactly throughout. The neutral coefficients were derived by semi-theory.

FIG. 1. Ionization potentials of the main groups in the limit of large row number of the periodic table, calculated using exact exchange, the local (spin) density approximation, and PBE; ETF denotes extended Thomas–Fermi theory.

FIG. 2. OEP ionization potential $I$ (in eV) vs $Z^{-1/3}$ for main groups of the periodic table. Also shown with green lines is the noble atoms LSDX curve.

TABLE I. Extrapolated ionization potentials $I$ (eV) of main group elements. Mean absolute differences (m.a.d.) are taken relative to OEP for X, and PBE for XC. The last two columns show the electron affinity $A$ (eV) (estimated as $I - 1/\langle r \rangle$ in atomic units) and the average radius $\langle r \rangle$ (bohr) of the ionization density, in the $Z \to \infty$ limit, using PBE. For ETF, $I = 3.15$ eV, $\langle r \rangle = 10.58$ bohr (Ref. 8), and $A = 0.58$ eV.

approximations of the density (LSD, PBE) and of the potential (OEP), used in the Engel code (see Ref. 20), give errors less than 0.1 eV for $I$. We use electronic configurations based on the Aufbau principle and Madelung rule. For the noble gases, $Z = n(n^2 + 6n + 14)/6 - \Delta(n)(n/2 + 1)$, where $n$ is the row number and $\Delta(n) = 0$ for even and 1 for odd rows. The greatest $n$ in our calculations is 25.

To understand in detail the results shown in Fig. 1, which are also tabulated in Table I, we begin at the exchange level. Both PBE and LSD exchange are almost identical to the OEP values for the $p$-group elements, with a maximum difference between them of 0.02 eV, and of either from OEP of 0.08 eV. This is not so for the alkalis and alkali earths, presumably because they have only one or two electrons outside a closed shell, with accompanying self-interaction error of approximate functionals. But, between group II (alkali
earth) and group III are the various transition series. Thus, in
the limit of large $Z$, the outer $p$ electrons of groups III–VIII
have orbitals that overlap strongly with those of many other
electrons.

In fact, Englert also showed that the TF result is not cor-
correct as $Z \to \infty$. The terms of $O(Z^{5/3})$ in Eq. (1) also yield
a finite contribution, which is included in ETF, yielding an $I$
of $3.15 \text{ eV}$, very close to the average over both $s$- and $p$-shell
values ($3.02 \text{ eV}$).

To check that this is no accident, consider the simpler
system of atoms with an infinitesimal electron–electron repul-
sion, $\lambda$, sometimes called Bohr atoms. The orbitals are
hydrogenic, requiring no self-consistency and simplifying
the integrals. One finds that $I_{\text{TF}}$ is exact for large $Z$ at
$\lambda = 0$. In Fig. 3, we show the exchange correction (divided
by $\lambda$) to $I$ for LSDX applied to the TF density [yielding
$8(2/3)^{1/3}/(3\pi^2) \approx 0.2360$], to the exact densities (each
averaged over entire shells), and exactly. All three match as
$Z \to \infty$, but a small error remains if, e.g., just the $s$-shell is
used. Thus we speculate that for real atoms, LSDX (in a KS
calculation) matches the average of exchange-only OEP over
an entire shell (including its transition series) as $Z \to \infty$.

Next, we discuss the DFT calculations with correlation,
which remains finite as $Z \to \infty$ and varies across a row. The
differences between PBE and LSD are relatively small, giv-
ning greater confidence in both. The maximum deviation be-
tween them for $p$-elements is $0.14 \text{ eV}$, comparable to the
deviations of these functionals at the exchange-only level from
OEP for the alkali and alkali earths. Thus the gradient cor-
rections are not vanishing, suggesting that while both calcula-
tions are accurate, neither is exact. The PBE average, $3.61 \text{ eV}$,
is our best estimate of a universal ionization potential, defined
as the limit of $I$ averaged over the $n$th shell, as $n \to \infty$.

The other major descriptor of chemistry is the electron
affinity $A(Z) = E_0(Z) - E_{-1}(Z)$. Within LSD or PBE,
the first negative atomic ion of energy $E_{-1}(Z)$ has no stable solu-
tion, but $A(Z)$ can still be estimated via a charged conductor
model, in which $I - A = 1/\langle r \rangle$, and $\langle r \rangle$ is the centroid of
the added charge. Define the radial ionization density as

$$
\Delta n_R(Z, r) = 4\pi r^2 (n_0(Z, r) - n_1(Z, r)),
$$

which integrates to $1$. Then choose $\langle r \rangle = \int_0^\infty dr r \Delta n_R(Z, r)$, as $Z \to \infty$ for
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expansion of Eq. (1) and a finite column-dependent $Z \to \infty$ limit for the ionization energy. It appears that LSD is extremely accurate and possibly exact in certain cases for $I$. Thus we have established that, in the large-$Z$ limit, the periodic table becomes perfectly periodic. Moreover, local approximations improve, even for energy differences that are relatively vanishingly small in this limit. These are new, numerically relevant, exact conditions that approximate functionals should satisfy.

All conclusions assume the Madelung rule for shell filling in groups I–VIII, and are based upon numerical calculations and extrapolation. Proving them rigorously is a challenge to mathematical physics. This work was supported by NSF (CHE-0809859) at Irvine, and NSF (DMR-0501588 and -0854769) at Tulane.