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Solution to the Kohn-Sham equations using reference densities from accurate, correlated wave functions for the neutral atoms helium through argon

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We solve the Kohn-Sham equations using the Zhao-Parr constraint potential within the Levy constrained-search method. Accurate exchange-correlation potentials, orbital energies, and components of the total energy including the Kohn-Sham kinetic energy T_s, the kinetic-energy contribution T_c to the exchange-correlation energy, and the exchange-correlation energy are calculated for the neutral atoms He through Ar. Reference densities used in the Zhao-Parr constraint potential are calculated from accurate, correlated, nonrelativistic wave functions. The exchange-correlation potentials exhibit characteristic intershell peaks, one for the atoms Li through Ne and two for the atoms Na through Ar.

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INTRODUCTION

Density functional models based on the Kohn-Sham equations are of great importance in producing approximate solutions to the problem of determining the structure of large molecular and solid-state systems. Much attention has been devoted to developing ever more accurate models for the exchange-correlation potential and the associated density functionals for calculating the exchange-correlation energy. As models for the exchange-correlation potential become more accurate and become better able to model electron correlation, it becomes necessary to have accurate numerical quantities against which new models can be tested and judged. Such accurate quantities have already been obtained for Be and Ne [1], the He isoelectronic sequence [2], the Be isoelectronic sequence [3], He and Ne [4], and He, Be, Ne, and Ar [5]. In this paper, we report accurate calculations of effective exchange-correlation potentials and accurate values of the Kohn-Sham kinetic energy T_s, the exchange-correlation energy E_{xc}, the kinetic-energy contribution T_c to E_{xc}, and the Kohn-Sham orbital energies ε_i using electron densities obtained from accurate nonrelativistic, correlated wave functions for the neutral atoms He through Ar.

A constrained-search [6,7] method for solving the exact Kohn-Sham equations when the density ρ_0 is known has been previously outlined [5,8,9]. The Kohn-Sham equations are expressed in the form

$$\left[-\tfrac{1}{2}\nabla^2+v_0(\mathbf{r})+\left[1-\frac{1}{N}\right]v_J^\lambda(\mathbf{r})+v_C^\lambda(\mathbf{r})\right]\Phi_i^\lambda(\mathbf{r}) =\epsilon_i^\lambda\Phi_i^\lambda(\mathbf{r}) \; , \qquad (1)$$

where the desired solution is for $\lambda\rightarrow\infty$. The potential v_0 is the external potential. The potential v_J^λ is the classical potential due to the charge density $\rho^\lambda(\mathbf{r})=\sum_i|\Phi_i^\lambda(\mathbf{r})|^2$:

$$v_J^\lambda(\mathbf{r})=\int\frac{\rho^\lambda(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' \; . \qquad (2)$$

The Fermi-Amaldi self-interaction correction [10] is included so that there will be less burden on v_C^λ and to give v_{xc} the correct long-range behavior. The potential v_C^λ is the functional derivative of the constraint, which forces ρ^λ to approach ρ_0 as the Lagrange multiplier λ approaches infinity. The constraint used is

$$C(\lambda)=\tfrac{1}{2}\int\int\frac{[\rho^\lambda(\mathbf{r}')-\rho_0(\mathbf{r}')][\rho^\lambda(\mathbf{r})-\rho_0(\mathbf{r})]}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}\,d\mathbf{r}' \qquad (3)$$

and the corresponding potential is

$$v_C^\lambda(\mathbf{r})=\lambda\int\frac{\rho^\lambda(\mathbf{r}')-\rho_0(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' \; . \qquad (4)$$

The angular integration of Eq. (4) is performed analytically for spherically symmetric atomic systems and the radial integral is evaluated numerically.

The exchange-correlation potential is

$$v_{\text{xc}}(\mathbf{r})=\lim_{\lambda\rightarrow\infty}\left[v_C^\lambda(\mathbf{r})-\frac{1}{N}v_J^\lambda(\mathbf{r})\right] \; . \qquad (5)$$

The exchange-correlation potential should decay at large r as $-1/r$ [11] and the term $-(1/N)v_J^\lambda(\mathbf{r})$ provides this correct long-range behavior. Numerical checks verify that v_{xc} calculated from Eq. (5) approach $-1/r$ at large r.

THE REFERENCE DENSITIES

The reference densities ρ_0 for Li and B through Ar were obtained from configuration interaction (CI) wave functions using basis sets of Slater type orbitals (STO's). The Li calculations were performed using the STO basis set from Jitrik and Bunge [12] and from Chakrovorty *et al.* [13]. The STO basis sets from Chakrovorty *et al.* [13] were combined with the STO's used by Clementi and

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Roetti [14] for the atoms B through Ar. Configuration interaction and self-consistent field calculations were performed using the ATOMCI [15] and ATOMSCF [16] computer programs, respectively, available in the MOTECC-90 package of programs. Densities obtained from the CI wave functions were scaled to satisfy the virial theorem where needed. Virial scaling affected most calculated quantities in the last one or two digits reported, except the total energy $E=-T$, which remained unchanged for all values reported except for the atoms Al and P.

The CI densities are spherically averaged and spin traced. The spherically averaged densities for P states correspond to ensemble averaged densities. For example, the density of the ^2P state for boron is

$$\rho(r)=\tfrac{1}{3}\rho^{+}(\mathbf{r})+\tfrac{1}{3}\rho^{0}(\mathbf{r})+\tfrac{1}{3}\rho^{-}(\mathbf{r}) \ , \tag{6}$$

where ρ^{-} is the density obtained from a wave function with $M_L=-1$, etc. These spherically averaged, spin-traced densities are used as the reference densities ρ_0 in the constraint potential v_C^{λ}.

The reference densities satisfy the nuclear cusp condition relatively well. The densities should decay at long range as [11,17–20]

$$\rho(r)\sim r^{2\beta}\exp(-2\alpha r) \ , \tag{7}$$

where $\alpha=(2V_{\text{ioniz}})^{1/2}$, V_{ioniz} is the ionization potential, and $\beta=(Z-N+1)/\alpha-1$. To check the long-range behavior of our CI densities, we have computed the quantity

$$\Delta=\frac{d\ln[\rho(r)]}{dr}-\left[\frac{2(1/\alpha-1)}{r}-2\alpha\right] . \tag{8}$$

The value of $|\Delta|$ at a density of 10^{-6} is fairly representative of $|\Delta|$ in the rest of the tail of the density. The values of $|\Delta|\le 0.1$ for atoms He, Li, Be, B, F, Na, Mg, Al, and S; $0.1<|\Delta|\le 0.4$ for N, Ne, and Si; and $0.4<|\Delta|<0.6$ for atoms C, O, Cl, and Ar.

CALCULATIONS AND RESULTS

The Kohn-Sham effective potential is found by solving Eq. (1) using either an extrapolation or iterative scheme. In the extrapolation scheme, Eq. (1) is solved with $\lambda=100$, 140, and 200, and extrapolating to $\lambda=\infty$. A quadratic extrapolation formula in $1/\lambda$ is used. In the iterative scheme, the constraint potential from each iteration step is incorporated as part of the known potential in subsequent steps. At each iteration step, a new unknown part of the constraint potential v_C^{λ} is found self-consistently. Iteration continues until the constraint, Eq. (3), is less than a specified tolerance, usually 10^{-7}. The total constraint potential $v_C^{\lambda=\infty}$ is the sum of the constraint potentials found at each step. The two schemes produce about the same results, with the magnitude of the difference less than 0.03 a.u. in T_s for the heavier atoms, except for Si where the magnitude of the difference in T_s was 0.06 a.u.

The radial parts of the Kohn-Sham orbitals are constructed from the orthogonal set

$$\phi_n^l=e^{-\mu r/2}r^lL_n^{2l+2}(\mu r), \quad n=0,1\ldots M-1 \ , \tag{9}$$

where μ is a scale factor chosen, where possible, to produce a calculated density ρ_λ that is within an order of magnitude of the reference density ρ_0 in the region $r=10$–15 a.u. Two values of μ were used for the heavier atoms, one for s orbitals and another value for the p orbitals. The L_n^{2l+2} are the Laguerre polynomials. The larger atoms have exchange-correlation potentials, which

TABLE I. Kohn-Sham orbital energies and the negative of the ionization potentials in atomic units. The exact ionization potentials V_{ioniz} are taken from Ref. [13].

Atom	1*s*	2*s*	2*p*	3*s*	3*p*	$-V_{\text{ioniz}}$
He[a]	−0.9039					−0.9037
Li	−2.085	−0.1998				−0.1981
Be[a]	−4.21	−0.338				−0.3424
B	−6.91	−0.516	−0.299			−0.305
C	−10.34	−0.726	−0.410			−0.4138
N	−14.44	−0.958	−0.528			−0.5340
O	−19.20	−1.141	−0.586			−0.5005
F	−24.66	−1.381	−0.684			−0.6402
Ne[b]	−30.82	−1.654	−0.797			−0.7923
Na	−38.08	−2.223	−1.183	−0.182		−0.189
Mg	−46.38	−3.080	−1.853	−0.259		0.281
Al	−55.61	−4.154	−2.734	−0.396	−0.214	−0.220
Si	−65.64	−5.406	−3.800	−0.621	−0.357	−0.300
P	−76.63	−6.621	−4.815	−0.684	−0.374	−0.3855
S	−88.32	−7.995	−5.990	−0.791	−0.416	−0.3807
Cl	−100.94	−9.504	−7.297	−0.932	−0.491	−0.4766
Ar	−114.43	−11.12	−8.704	−1.058	−0.547	−0.5792

[a] Reference [5].

[b] The neon values are computed with a wave function that is slightly improved over the one used in Ref. [5].

TABLE II. The CI energies, exact energies, and components of the energy (in a.u.). The exact energies are taken from Ref. [13] except for the He value, which is from Ref. [21].

Atom	E_{calc}	E_{exact}	J	$\langle -Z/r \rangle$	T_s	T_c	E_{exc}	$\int \rho v_{\mathrm{xc}} d\mathbf{r}$
He[a]	−2.9037	−2.9037	2.050	−6.753	2.867	0.037	−1.068	−2.021
Li	−7.4779	−7.4781	4.067	−17.154	7.44	0.038	−1.827	−2.787
Be[a]	−14.6669	−14.6674	7.220	−33.708	14.59	0.074	−2.772	−4.429
B	−24.6499	−24.654	11.647	−56.98	24.56	0.095	−3.87	−6.028
C	−37.8415	−37.845	17.856	−88.21	37.72	0.12	−5.21	−8.171
N	−54.5814	−54.589	26.178	−128.41	54.43	0.15	−6.78	−10.68
O	−75.0537	−75.067	36.637	−178.12	74.86	0.19	−8.43	−13.02
F	−99.7164	−99.734	49.830	−238.70	99.47	0.24	−10.32	−15.94
Ne[b]	−128.926	−128.94	66.086	−311.15	128.63	0.30	−12.49	−19.39
Na	−162.24	−162.25	80.030	−389.76	161.92	0.31	−14.44	−20.08
Mg	−200.024	−200.05	95.901	−479.18	199.69	0.34	−16.43	−22.85
Al	−242.295	−242.35	112.95	−578.65	241.94	0.35	−18.53	−26.12
Si	−289.276	−289.36	133.36	−690.70	288.92	0.36	−20.86	−31.79
P	−341.172	−341.26	153.69	−812.47	340.76	0.41	−23.15	−33.59
S	−397.991	−398.11	177.24	−947.21	397.60	0.39	−25.62	−36.65
Cl	−460.004	−460.15	203.33	−1094.74	459.59	0.41	−28.19	−40.46
Ar	−527.388	−527.54	232.21	−1255.86	527.17	0.21	−30.91	−44.45

[a]Reference [5].

[b]The neon values are computed with a wave function that is slightly improved over the one used in Ref. [5].

are fairly deep near the nucleus where the density is high. Higher values of μ help the convergence of Eq. (1) for the atoms with larger atomic number. Unfortunately, these higher values of μ sometimes result in ρ^{λ}, which differ from ρ_0 at large r by more than an order of magnitude.

There are three possible sources of errors in these calculations. First, there are the reference densities themselves. The densities for He, Li, and Be are very nearly the exact densities, but the others are not, even though they are calculated from relatively accurate CI wave functions. The error due to inexact densities is probably the greatest source of error in these calculations. The second source of error is in the choice of the basis sets used for the Kohn-Sham orbitals. A basis set that has a high μ needed for convergence of Eq. (1) when the density is high near the nucleus may not be the best one for obtaining the correct long-range behavior. The third possible source of error is in the extrapolation or iterative procedures; we believe these are small.

The Kohn-Sham orbital energies are reported in Table I. The orbital energy of the highest occupied orbital is nearly equal to the negative of the exact ionization potential for the lighter atoms where the densities are more accurate; they are relatively close even for the heavier atoms where the densities are not quite as accurate. We expect more accurate ionization potentials will be found

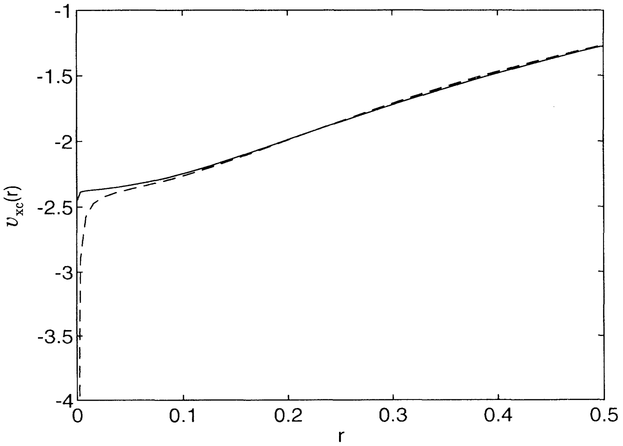

FIG. 1. The exchange-correlation potentials (in a.u.) for Li using the JB basis is the solid line, and using the CGDPF basis is the dashed line.

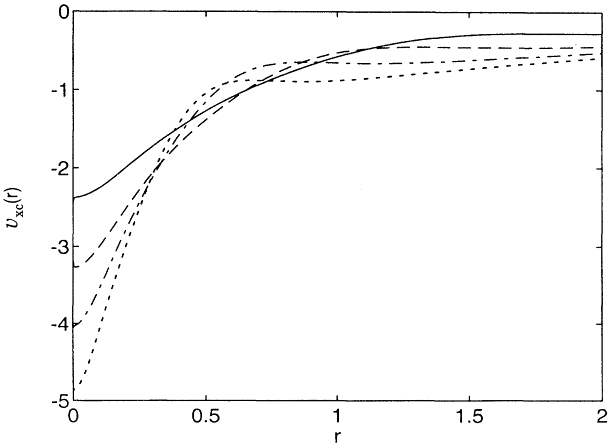

FIG. 2. The exchange-correlation potential (in a.u.) for atoms Li through C. Li is the solid line; Be is the long dashed line; B is the alternating long and short dashed line; C is the short dashed line.

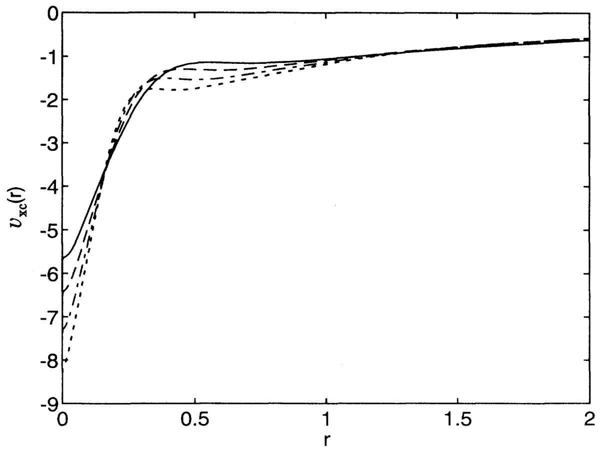

FIG. 3. The exchange-correlation potential (in a.u.) for N through Ne. N is the solid line; O is the long dashed line; F is the alternating long and short dashed line; Ne is the short dashed line.

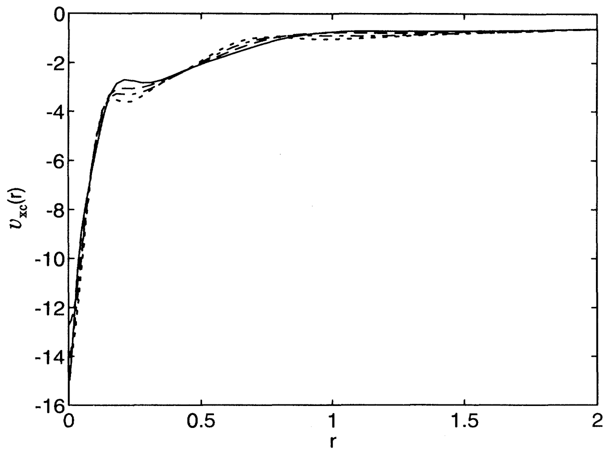

FIG. 5. The exchange-correlation potential (in a.u.) for P through Ar. P is the solid line; S is the long dashed line; Cl is the alternating long and short dashed line; Ar is the short dashed line.

when higher quality densities are used as the reference.

The constrained-search quantities of interest are in the energy expression

$$E = T_s + E_{en} + J + E_{xc} , \tag{10}$$

where T_s is the Kohn-Sham kinetic energy, E_{en} is the electron-nuclear attraction energy, J is the Coulomb energy, and E_{ex} is the exchange-correlation energy. In addition, we have computed T_c, the kinetic-energy contribution to E_{xc}, and the quantity $\int \rho(r) v_{xc}(r) d\mathbf{r}$. The CI energy is used in the calculation of the exchange-correlation energy E_{xc}.

The energy components are reported in Table II. We believe the reported values of T_s, T_c, and E_{xc} are very near the exact ones for the lighter atoms. These do not have significant errors due to basis set selection for the atoms through Mg. Based on calculations using different values of μ and different numbers of basis functions, we estimate there are basis set errors for atoms Al through Ar with the error increasing to around ±0.1 a.u. in T_s for Cl and Ar. The quantity T_c is computed as the relatively small difference between two numbers that are two or three orders of magnitude larger than it. Its values are sensitive to basis set selection and the density for the heavier atoms. Consequently, the values of T_c reported for the heavier atoms are less accurate than for the lighter atoms.

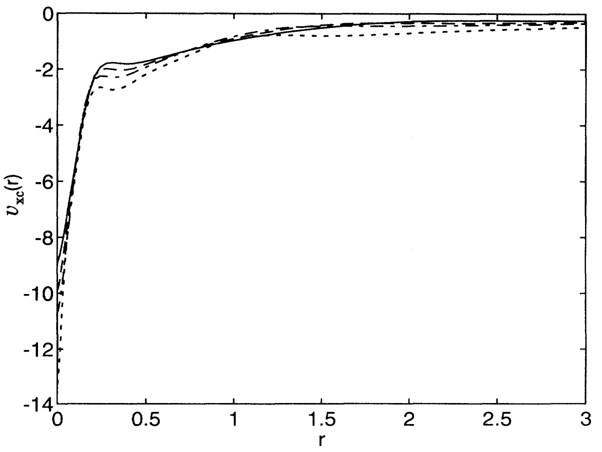

FIG. 4. The exchange-correlation potential (in a.u.) for Na through Si. Na is the solid line; Mg is the long dashed line; Al is the alternating long and short dashed line; Si is the short dashed line.

The Li CI calculations were performed using two different basis sets: the STO basis set of Jitrik and Bunge (JB) [12], and the STO basis set of Chakravorty *et al.* (CGDPF) [13]. The JB basis set produced the best total energy and presumably the most accurate exchange-correlation potential. In Fig. 1, the two potentials are shown near the nucleus. The exchange-correlation potential in the CGDPF basis set exhibits an apparent anomaly by plunging sharply at small r. This is diminished in the exchange-correlation potential using the more accurate density obtained with the JB basis. The only differences between the two calculations are the densities computed from the two different CI wave functions. A similar probably anomalous plunge is present in our previous He results [5] and is not present in the He exchange-correlation potential of Umrigar and Gonze [2]. Formal analysis of the exchange-correlation potential for two-electron systems indicates that it is finite near the nucleus [20,22]. This has been verified by numerical calculations [2,4,5]. The present work and previous numerical calculations [3–5] suggest, though do not prove, that the exchange-correlation potential is finite near the nucleus for systems with more than two electrons.

The exchange-correlation potentials are shown in Fig. 2 for the atoms Li through C, in Fig. 3 for the atoms N through Ne, in Fig. 4 for the atoms Na through Si, and in Fig. 5 for the atoms P through Ar. The v_{xc} exhibit characteristic peaks in the intershell regions: one peak for Li-Ne and two for Na-Ar. The maxima in v_{xc} for Na occur at $r = 0.31$ and 2.53 a.u.

CONCLUSIONS

We have computed a number of total energy components that are of interest in developing density functional models. The exchange-correlation potentials and the energy components for the lighter atoms are expected to be near the exact ones, with some decrease in accuracy for the heavier atoms. It is our hope that these computed quantities will aid in the search for better exchange-correlation potentials.

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[1] R. van Leeuwen and E. T. Baerends, Phys. Rev. A **49**, 2421 (1994).

[2] C. J. Umrigar and X. Gonze, Phys. Rev. A **50**, 3827 (1994).

[3] J. Chen, R. O. Esquivel, and M. J. Stott, Philos. Mag. B **69**, 1001 (1994).

[4] C. J. Umrigar and X. Gonze, in *High Performance Computing and its Applications to the Physical Sciences*, Proceedings of the Mardi Gras '93 Conference, edited by D. A. Browne *et al.* (World Scientific, Singapore, 1993).

[5] Q. Zhao, R. C. Morrison, and R. G. Parr, Phys. Rev. A **50**, 2138 (1994).

[6] M. Levy, Proc. Natl. Acad. Sci. U.S.A. **76**, 6062 (1979).

[7] M. Levy and J. P. Perdew, in *Density Functional Methods in Physics*, edited by R. M. Dreizler and J. da Providencia (Plenum, New York, 1985), pp. 11–30.

[8] Q. Zhao and R. G. Parr, Phys. Rev. A **46**, 2337 (1992).

[9] Q. Zhao and R. G. Parr, J. Chem. Phys. **98**, 543 (1992).

[10] E. Fermi and E. Amaldi, Acad. Ital. Rome **6**, 117 (1934).

[11] C. O. Ambladh and U. von Barth, Phys. Rev. B **31**, 3231 (1985).

[12] O. Jitrik and C. F. Bunge, Phys. Rev. A **43**, 5804 (1991).

[13] S. J. Chakravorty, S. R. Gwaltney, E. R. Davidson, F. A. Parpia, and C. Froese Fischer, Phys. Rev. A **47**, 3649 (1993).

[14] E. Clementi and C. Roetti, At. Data Nucl. Data Tables **14**, 177 (1974).

[15] F. Saski, M. Sekiya, T. Noro, K. Ontsuki, and Y. Osanai, in *Modern Techniques in Computational Chemistry*, edited by E. Clementi (ESCOM, Leiden, 1990), p. 181.

[16] E. Clementi, *Modern Techniques in Computational Chemistry* (ESCOM, Leiden, 1990).

[17] M. Hoffman-Ostenhof and T. Hoffman-Ostenhof, Phys. Rev. A **16**, 1782 (1977).

[18] R. Ahlrichs, M. Hoffman-Ostenhof, T. Hoffman-Ostenhof, and J. D. Morgan III, Phys. Rev. A **23**, 2106 (1981).

[19] J. Katriel and E. R. Davidson, Proc. Natl. Acad. Sci. U.S.A. **77**, 4403 (1980).

[20] M. Levy, J. P. Perdew, and V. Sahni, Phys. Rev. A **30**, 2745 (1984).

[21] D. E. Freund, B. D. Huxtable, and J. D. Morgan III, Phys. Rev. A **29**, 980 (1984).

[22] E. R. Davidson, Int. J. Quantum Chem. **37**, 811 (1990).