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Hartree-Fock densities in Thomas-Fermi-Dirac formulas including the inhomogeneity term

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Hartree-Fock-Roothaan-Clementi (HFRC) densities are used to calculate the total kinetic energies and the total binding energies of neutral atoms according to the Thomas-Fermi-Dirac formulas with inhomogeneity corrections. The strength of the Weizsäcker inhomogeneity correction is multiplied by the Kompaneets and Pavlovskii, and Kirzhnits factor of 1/9. Of the atoms considered ($Z = 2$ to $Z = 36$; $Z = 54$) almost all the total kinetic energies agree with the HFRC expectation values to better than 1%, and the largest disagreement is 1.7%. Except for He, Li, Be, and B, the total binding energies agree with the HFRC expectation values to better than 0.7%. Higher-order corrections of the Thomas-Fermi-Dirac-Weizsäcker formulas are therefore very small.

The use of Hartree-Fock (HF) densities in Thomas-Fermi-Dirac (TFD) formulas is not new. Especially in a complicated atomic system, a TFD formula is often used as an initial approximation for simplifying the calculations. For example, in the Hartree-Fock-Slater formulation,[1] the exchange term was replaced by the Dirac exchange contribution according to the TFD formula. Recently, the HF densities were also applied in TFD formulas to calculate the intermolecular forces.[2] The simplicity and the apparent success of this model has brought a renewed interest in these approximations. To justify the approximations, the same model was later tested for the individual atoms.[3] The results of the TFD total binding energy $E(\mathrm{TF})$ were, in general, within 10% of the exact HF values $E(\mathrm{HF})$. This remarkable agreement has been considered as an important supporting factor for the proposed scheme "electron-gas approximation."

In order to test the internal consistency between the HF and the TFD formulation and to be convinced that the apparent agreement is not accidental, it is necessary to carry out the estimate to the next order. In 1935 Weizsäcker introduced the quantum inhomogeneity correction

$$W = \frac{1}{8} \int \frac{|\nabla\rho|^2}{\rho}\, dv$$

(in atomic units).[4] Starting from the HF formula, Kompaneets and Pavlovskii, and later Kirzhnits[5] concluded that $\frac{1}{9}W$ and the Dirac exchange contribution $J(\mathrm{D})$ should be considered together as the semi-quantum-mechanical correction of the HF model to second order in $\hbar$.

There have been many analyses on the total energy, the diamagnetic susceptibility, and the atomic polarizability of the extended TFDW formulation.[6] In some applications, the TFDW formula is restricted to the intermediate region of r.[7] Others use a Weizsäcker correction with an adjustable strength parameter λ.[8] The empirical value thus obtained from a variational TFDW calculation of the noninteracting electrons was found to be $\lambda = 0.2$ instead of the Kompaneets and Pavlovskii, and Kirzhnits factor of $\lambda = \frac{1}{9}$, although the physical meaning of such strength factors is unclear. So far the consistency between the HF and the TFDW solutions has never been tested systematically. We have, therefore, extended the calculation of Ref. 1 to evaluate the TFDW energy for all the neutral atoms up to krypton using the same input Hartree-Fock-Roothaan-Clementi (HFRC) densities.[9] To simplify the calculation, the input density, ρ_{in} for the open-shell atoms, is approximated by averaging the ρ_{HF} over the solid angle. Since we are primarily interested in the consistency between the HF and the TFDW formulation, this input density ρ_{in} has not been subjected to variation. Results are summarized in Table I. The same calculation is also made for the revised HFRC densities[10] for the light elements and the closed-shell atoms up to Kr. The results obtained are the same as before, and are therefore not presented. However, the additional result on Xe is included in Table I.

If we treat $\frac{1}{9}W$ as the inhomogeneity correction for the TF kinetic energy $K(\mathrm{TF})$, the resultant values are in remarkable agreement with the corresponding HF kinetic energy $K(\mathrm{HF})$. Even including the light elements such as He, the relative error is less than 1.7%. Alternatively, we may consider $\frac{1}{9}W + J(\mathrm{D})$ as the correction to the TF model. Since the HF exchange energy $J(\mathrm{HF})$ is not given explicitly, it is estimated by subtracting the Coulomb energy U calculated with ρ_{in} from the tabulated HF potential energy. This is equivalent to considering $E(\mathrm{TFDW}) = K(\mathrm{TF})$

TABLE I. Comparison between the Thomas-Fermi-Dirac-Weizsäcker (TFDW) and Hartree-Fock (HF) methods, with Roothaan-Clementi densities (1965). Repeated entries for the same element refer to different multiplet terms arising from the ground-state configuration. All numbers are in atomic units.

A	K(TF)	$W/9$	K(HF)	ERR% [a]	J(D)	J(HF)	ERR% [b]	E(TFDW)	E(HF)	ERR% [c]
He	2.56	0.32	2.86	0.6	−0.9	−1.0	−14	−2.70	−2.86	−5.5
Li	6.68	0.80	7.43	0.6	−1.5	−1.8	−15	−7.12	−7.43	−4.2
Be	13.13	1.52	14.57	0.5	−2.3	−2.7	−13	−14.14	−14.57	−2.9
B	21.97	2.43	24.53	−0.5	−3.3	−3.8	−13	−24.17	−24.53	−1.5
C	33.61	3.55	37.63	−1.3	−4.4	−5.0	−12	−37.51	−37.63	−0.3
C	33.65	3.55	37.69	−1.3	−4.4	−5.0	−13	−37.53	−37.69	−0.4
C	33.56	3.56	37.55	−1.2	−4.4	−4.9	−10	−37.48	−37.55	−0.2
N	48.63	4.87	54.40	−1.7	−5.8	−6.6	−13	−54.45	−54.40	0.1
N	48.55	4.87	54.30	−1.6	−5.7	−6.5	−12	−54.43	−54.30	0.3
N	48.49	4.87	54.23	−1.6	−5.7	−6.4	−11	−54.42	−54.23	0.3
O	67.14	6.40	74.73	−1.6	−7.3	−8.1	−10	−75.09	−74.73	0.5
O	67.22	6.39	74.81	−1.6	−7.3	−8.2	−11	−75.10	−74.81	0.4
O	67.03	6.40	74.61	−1.6	−7.2	−7.9	−9	−75.08	−74.61	0.6
F	90.06	8.13	99.41	−1.2	−9.0	−10.0	−10	−99.65	−99.41	0.2
Ne	117.8	10.1	128.5	−0.5	−11	−12	−9	−128.2	−128.5	−0.3
Na	148.8	12.3	161.8	−0.5	−13	−14	−9	−161.4	−161.8	−0.3
Mg	184.0	14.7	199.6	−0.4	−15	−16	−9	−199.1	−199.6	−0.3
Al	223.4	17.4	241.9	−0.4	−17	−18	−9	−241.4	−241.9	−0.2
Si	267.1	20.3	288.8	−0.5	−19	−20	−9	−288.4	−288.8	−0.1
Si	267.1	20.3	288.8	−0.5	−19	−20	−9	−288.4	−288.8	−0.1
Si	267.1	20.3	288.8	−0.5	−19	−20	−8	−288.4	−288.8	−0.1
P	315.5	23.5	340.7	−0.5	−21	−23	−9	−340.4	−340.7	−0.1
P	315.5	23.5	340.6	−0.5	−21	−23	−9	−340.4	−340.6	−0.1
P	315.4	23.5	340.6	−0.5	−21	−23	−8	−340.4	−340.6	−0.0
S	368.6	26.8	397.5	−0.5	−23	−25	−8	−397.4	−397.5	−0.0
S	368.5	26.8	397.4	−0.5	−23	−25	−8	−397.4	−397.4	0.0
S	368.5	26.8	397.4	−0.5	−23	−25	−8	−397.4	−397.4	0.0
Cl	426.7	30.4	459.5	−0.5	−25	−28	−8	−459.6	−459.5	0.0
Ar	489.9	34.3	526.8	−0.5	−28	−30	−8	−527.0	−526.8	0.0
K	557.5	38.3	599.2	−0.5	−30	−33	−8	−599.8	−599.2	0.1
Ca	630.0	42.7	676.8	−0.6	−33	−35	−8	−678.0	−676.8	0.2
Sc	707.3	47.2	759.7	−0.7	−35	−38	−8	−762.0	−759.7	0.3
Ti	789.9	51.9	848.4	−0.8	−38	−41	−8	−851.9	−848.4	0.4
V	878.0	56.8	942.9	−0.9	−41	−44	−8	−947.6	−942.9	0.5
Cr	971.8	62.0	1043	−0.9	−44	−48	−8	−1049	−1043	0.6
Mn	1072	67.4	1150	−0.9	−47	−51	−8	−1157	−1150	0.6
Fe	1177	73.0	1262	−1.0	−51	−55	−7	−1271	−1262	0.6
Co	1289	78.8	1381	−1.0	−54	−58	−7	−1391	−1381	0.7
Ni	1408	84.8	1507	−0.9	−58	−62	−7	−1517	−1507	0.7
Cu	1533	91.1	1639	−0.9	−62	−66	−6	−1649	−1639	0.6
Cu	1533	91.1	1639	−0.9	−62	−66	−6	−1649	−1639	0.6
Zn	1666	97.6	1778	−0.8	−66	−70	−6	−1788	−1778	0.6
Ga	1804	104	1923	−0.8	−69	−74	−6	−1934	−1923	0.5
Ge	1948	111	2075	−0.8	−73	−78	−6	−2086	−2075	0.5
Ge	1948	111	2075	−0.8	−73	−78	−6	−2086	−2075	0.5
As	2099	119	2234	−0.8	−77	−82	−6	−2246	−2234	0.5
As	2099	119	2234	−0.8	−77	−82	−6	−2246	−2234	0.5
As	2099	119	2234	−0.8	−77	−82	−6	−2246	−2234	0.5
Se	2256	126	2400	−0.7	−81	−86	−6	−2412	−2400	0.5
Se	2256	126	2400	−0.7	−81	−86	−6	−2412	−2400	0.5
Se	2256	126	2400	−0.7	−81	−86	−6	−2412	−2400	0.5
Br	2420	134	2572	−0.7	−85	−90	−6	−2585	−2572	0.5
Kr	2591	142	2752	−0.7	−89	−95	−6	−2765	−2752	0.5
Xe [d]	6857	326	7232	−0.7	−171	−181	−6	−7270	−7232	0.5

[a] ERR% = $\{[K(\mathrm{TF}) + W/9]/K(\mathrm{HF}) - 1\} \times 100\%$.

[b] ERR% = $[J(D)/J(\mathrm{HF}) - 1] \times 100\%$.

[c] ERR% = $[E(\mathrm{TFDW})/E(\mathrm{HF}) - 1] \times 100\%$.

[d] From the revised Roothaan-Clementi densities (1974), Ref. 10.

$+\frac{1}{9}W+J(\mathrm{D})+U$ as an approximation to the $E(\mathrm{HF})$. Except for the light elements He, Li, Be, and B, the E(TFDW) is in even better agreement with the E(HF) than the K(TFDW) is with K(HF). The relative error is less than 0.7%! The sign of the errors is also correlated with the shell structure. Considering the simplicity and the crudeness of the TFDW formulation, this general consistency is surprisingly excellent.

The general agreements between the TFDW evaluations and the exact HF values for the neutral atoms strongly suggest that not only is $\frac{1}{9}W+J(\mathrm{D})$ the consistent semi-quantum-mechanical correction of the TF model but also that the higher-order corrections are small. Since the inhomogeneity correction $\frac{1}{9}W$ is usually larger than the exchange contribution $J(\mathrm{D})$, an extension of the TF model without this correction would introduce sizable error. We are presently examining the effects of the inhomogeneity term on the rare-gas interaction potentials.[11]

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