Relativistic density functional theory with finite-light-speed correction for the Coulomb interaction: a non-relativistic-reduction-based approach

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Abstract
The Breit correction, the finite-light-speed correction for the Coulomb interaction of the electron–electron interaction in $O\left(1/c^2\right)$, is introduced to density functional theory (DFT) based on the non-relativistic reduction with the local density approximation. Using this newly developed relativistic DFT, it is found that the possible outer-most electron of lawrencium atom is the $p$ orbital instead of the $d$ orbital, which is consistent with the previous calculations based on wave-function theory. A possible explanation of the anomalous behavior of its first ionization energy is also given. This DFT scheme provides a practical calculation method for the study of properties of super-heavy elements.

Keywords: relativistic density functional theory, super-heavy elements, finite-light-speed effects, Breit interaction

(Some figures may appear in colour only in the online journal)

1. Introduction
The periodic table of the elements, one of the most fundamental information for general science, is determined by the electronic configuration, and represents periodicity of fundamental atomic properties, such as the ionization energy and the electron affinity [1]. Recently, super-heavy elements (SHEs), such as nihonium ($Z = 113$) [2], moscovium ($Z = 115$) [3], tennessine ($Z = 117$) [4, 5], and oganesson ($Z = 118$) [6], were synthesized. Syntheses of heavier elements are still ongoing. However, the positions of the SHEs in the periodic table are yet tentative since their chemical properties have not been established.

A recent experimental measurement of the first ionization energy of lawrencium ($Z = 103$) [7] casts doubt on the current placement of the SHEs in the periodic table. The measured value does not follow the tendency of the other 5$f$-block elements, which is common to the ionization energy of lutetium ($Z = 71$) among the 4$f$-block elements. In addition, compared with the vertically neighboring elements in the 4$f$ and 5$f$ blocks, the first ionization energy of lawrencium is smaller than that of lutetium, whereas those of the other 5$f$-block elements are larger than those of the corresponding 4$f$-block elements, respectively. With these anomalous features of lawrencium—we refer to this as ‘the puzzle of lawrencium’—it has been discussed in IUPAC [8] whether the suitable places of lawrencium and lutetium are the $f$ or $d$ block. In fact, a previous theoretical calculation assuming the electronic configurations referring to the current periodic table did not present these features [9].

The results mentioned above indicate that the position of the SHEs on the current periodic table may not generally reflect...
the actual electronic configurations in their atomic forms and their properties. Due to short half-lives of the SHEs, first-principles numerical simulations are essential tools complementary to experiments for understanding properties of SHEs.

It is known that the relativistic effects are non-negligible in such large Z atoms [10–12]. The relativistic effects in electronic systems come from two origins: (1) difference between the Schrödinger and the Dirac Hamiltonians and (2) the correction to the Coulomb interaction. The lowest order of relativistic effects incorporated by using the Dirac equation instead of the Schrödinger equation is \( O((\text{Ze})^2) \sim O(1/c^2) \). Here, \( \alpha = e^2/(4\pi\varepsilon_0\hbar c) \approx 1/137 \) is the fine-structure constant. Once the relativistic effect incorporated by the Dirac equation is considered, the Breit correction between two electrons, which will be explained later, should also be considered to keep consistency of the order of \( Z\alpha \).

The relativistic effect due to the correction to the Coulomb interaction can be derived by the quantum electrodynamics (QED) through the two-body scattering amplitude [13]. After the calculation of the quantum field theory in the Coulomb gauge (\( \text{div} \mathbf{A} = 0 \)), in the atom with the atomic number \( Z \), the electron–electron interaction with \( O((\text{Ze})^2) \) is called the Breit correction [14, 15], whereas the Coulomb interaction between two electrons is \( O(\text{Ze}) \). The Breit correction is also called the relativistic effect or the finite-light-speed effect. The higher-order terms than the Breit correction are called the QED effects, which are \( O((\text{Ze})^n\alpha^m) \) with \( n \geq 2 \) and \( m \geq 1 \), and it is \( \alpha \) times or much smaller than the Breit correction [10].

Note that the relativistic correction of the Coulomb potential due to the atomic nucleus is \( O((\text{Ze})^n\alpha^m(m_e/M_{\text{Nuc}})^{l}) \) with \( n \geq 2 \), \( m \geq 1 \), and \( l \geq 1 \), where \( m_e \) and \( M_{\text{Nuc}} \) are the masses of electrons and atomic nuclei, respectively, and because of \( m_e/M_{\text{Nuc}} < 1/1000 \), this effect is negligible [10].

The first-principles approaches to the electronic properties are classified into two groups: wave-function theory and density functional theory (DFT) [16–18]. The electronic structure calculation based on wave-function theory with the relativistic effects in \( O(1/c^2) \) has been performed [19–25]. There, ‘the puzzle of lawrencium’ has also been addressed [38–41]. The exchange–correlation functionals have been proposed with the \( \text{ab initio} \) local density approximation (LDA) [40, 42] and the empirical generalized gradient approximation (GGA) [43]. Relativistic extension of the optimized potential method [44, 45], the Dirac DFT with the elimination of the small component [46], and the current–current interaction [47, 48] have also been established.

In this paper, we take another route to develop a DFT for the relativistic effects. The non-relativistic reduction of the original Hamiltonian is first performed, and the Kohn–Sham Hamiltonian is constructed from the reduced Hamiltonian, instead of the methods adopted in previous works. This DFT scheme starts from the same Hamiltonian as the wave-function methods for discussion of the electronic structure of SHEs. Hence, fair comparison with the results of the wave-function method is feasible.

Moreover, the way to construct the DFT scheme is parallel to the conventional non-relativistic (Non-rel) LDA in the PZ81 functional [49]. The LDA exchange–correlation energy for the reduced Hamiltonian with the relativistic effects up to \( O(1/c^2) \) has been calculated with an accurate numerical solver by Kenny et al [42]. On top of this, we complete the \( O(1/c^2) \) LDA by formulating the Hartree term for the Breit correction to the electron–electron interaction. Thanks to this formulation, the relativistic correction is given as additional terms on top of the Non-rel DFT. Hence, one can compare the results of the relativistic scheme with those of the Non-rel scheme clearly.

It is known that the LDA, even in the Non-rel DFT, can give erroneous results already for the lighter elements including 3d-electron systems [50–54], which is admittedly cured by the gradient [41, 55, 56], the discontinuity of the exchange–correlation potential \( V_{\text{xc}} \) [56–60] and self-interaction corrections [49, 61, 62]. Nevertheless, we expect that our LDA-based scheme is efficient for heavy elements, since the correction to the exchange energy by those become irrelevant in the large Z regime [63], and it is still meaningful to use atomic systems as benchmark calculations.

This paper is organized as follows: first, in section 2, the theoretical framework of DFT with the Breit correction is introduced. Then, in sections 3.1 and 3.2, all-electron calculation of selected atoms are performed as a benchmark. In section 3.3, the possible reason for ‘the puzzle of lawrencium’ is suggested, with performing all-electron calculation of lutetium and lawrencium atoms. Finally, in section 4, the conclusion and perspectives of this paper are shown. In appendix A, the detailed discussion about the relativistic exchange–correlation functional is shown, and in appendix B, derivation of the relativistic Hartree term is shown.

2. Theoretical framework

In this section, the relativistic DFT with the Breit correction is formulated. We start from the Dirac equation instead of the Schrödinger equation, where the Breit correction is considered in the electron–electron interaction \( V_{\text{int}} \). To use the Kohn–Sham scheme, the Hartree term \( E_{\text{H}} \) and the
exchange–correlation functional $E_{xc}$ should be reconstructed, since $V_{\text{int}}$ is no longer the original Coulomb interaction.

In this paper, the Hartree atomic unit is used, i.e., $m_e = h = 4\pi\varepsilon_0 = \varepsilon^2 = 1$ and $c = 1/\alpha$, and the Coulomb–Breit interaction refers to the electron–electron interaction with the Breit correction as well as the Coulomb interaction.

### 2.1. Original Hamiltonian

In general, the Dirac Hamiltonian in quantum many-body problems reads

$$\hat{H} = \hat{T} + \sum_j V_{\text{ext}}(r_j) + \sum_{j<k} V_{\text{int}}(r_j, r_k),$$

(1)

where $\hat{T}$ is the kinetic operator, $V_{\text{ext}}$ is the external potential, and $V_{\text{int}}$ is the interaction between electrons. Note that the Hamiltonian (1) operates on the Dirac spinor and $\hat{T}$ is the Dirac kinetic operator $\hat{T}^D$ instead of the Schrödinger kinetic operator $\hat{T}$. The Dirac kinetic operator $\hat{T}^D$ is written in sum of the single-particle Dirac kinetic operator for electrons $\hat{p}_j^D$:

$$\hat{T}^D = \sum_j \hat{p}_j^D,$$

(2)

where

$$\hat{p}_j^D = \beta j \mathbf{e}^2 + c \mathbf{\alpha}_j \cdot \mathbf{p}_j.$$  

(3)

Here, $\mathbf{\alpha}_j$ and $\beta_j$ are the Dirac matrices for the $j$th electron,

$$\mathbf{\alpha} = \begin{pmatrix} O_2 & \sigma_z \\ \sigma_z & O_2 \end{pmatrix}, \begin{pmatrix} O_2 & \sigma_y \\ \sigma_y & O_2 \end{pmatrix}, \begin{pmatrix} O_2 & \sigma_x \\ \sigma_x & O_2 \end{pmatrix},$$

$$\beta = \begin{pmatrix} I_2 & 0 \\ 0 & -I_2 \end{pmatrix},$$

(4)

where $\sigma_x$, $\sigma_y$, and $\sigma_z$ are the Pauli matrices, and $O_2$ and $I_2$ are the $2 \times 2$ zero and identity matrices, respectively.

The Coulomb–Breit interaction

$$V_{\text{int}}(r_j, r_k) = \frac{1}{r_{jk}} - \frac{c \mathbf{\alpha}_j \cdot \mathbf{p}_j}{2c^2 r_{jk}} + \frac{c \mathbf{\alpha}_j \cdot \mathbf{r}_k}{2c^2 r_{jk}} \frac{c \mathbf{\alpha}_k \cdot \mathbf{r}_j}{2c^2 r_{jk}}$$

(5)

is adopted for the electron–electron interaction $V_{\text{int}}$, where $r_{jk} = |r_j - r_k|$. The first term is the original Coulomb interaction and the second term is the Breit correction [14, 15]. The kinetic operator for the nuclei is neglected, and $V_{\text{int}}$ is the interaction between the atomic nucleus and electrons. Only the Coulomb interaction is considered for $V_{\text{int}}$, since the finite-light-speed correction to $V_{\text{int}}$ is proportional to $m_e/M_{\text{nuc}}$ much smaller than that to $V_{\text{int}}$ [10]:

$$V_{\text{ext}}(r_j) = -\frac{Z}{r_j}.$$  

(6)

### 2.2. Non-relativistic reduction

As mentioned in section 1, the Kohn–Sham Hamiltonian is constructed after the non-relativistic reduction of the original Dirac Hamiltonian (1), instead of the method used in the previous works.

According to the Hohenberg–Kohn theorem [16], the universal functional $F$ of the electron density $\rho$ with respect to the kinetic operator $\hat{T}$ and the interaction $V_{\text{int}}$ gives the ground-state energy of the Hamiltonian via

$$E[\rho] = F[\rho] + \int \rho(r) V_{\text{ext}}(r) \, dr.$$  

(7)

The exchange–correlation energy functional $E_{xc}$ is defined with this $F$, as mentioned later. The standard functionals, such as the PZ81 [49] and PBE [55] functionals, are applicable only to the Schrödinger scheme. In the present case, the exchange–correlation functional should be reconstructed on the basis of the Dirac Hamiltonian.

Since only positive-energy states are usually interested, non-relativistic reduction of the Hamiltonian is used for this scheme. One of the most widely used non-relativistic reduction methods is the Foldy–Wouthuysen transformation [64–67]. The Foldy–Wouthuysen transformation of the Hamiltonian given in equation (1) derived by Kenny et al [68] is

$$\hat{H}_{FW} = \hat{T}^S + \sum_j V_{\text{ext}}(r_j)$$

$$+ \sum_j \left\{ V_1(r_j, s_j) - \frac{Z}{2c^2 r^2_j} s_j \cdot [r_j \times \nabla] \right\}$$

$$+ \sum_{j<k} V_2(r_j, r_k, s_j, s_k),$$

(8)

where the correction terms $V_1$ and $V_2$ read

$$V_1(r_j, s_j) = -\frac{\nabla^4}{8c^2} + \frac{Z \pi}{2c^2} \delta(r_j),$$

(9)

$$V_2(r_j, r_k, s_j, s_k) = -\sum_{j<k} \frac{\pi}{2c^2} \delta(r_j - r_k) - \sum_{j<k} \frac{1}{r^2_{jk}} \nabla_k$$

$$\cdot \left[ \frac{1}{r_{jk}} + \frac{r_j - r_k}{r^2_{jk}} \right] \nabla_j s_j \cdot s_k,$$

$$- \frac{8 \pi}{c^2} \delta(r_j - r_k) s_j \cdot s_k$$

$$- \sum_{j<k} \frac{1}{c^2} \nabla_j \cdot \left[ 3 (r_j - r_k) (r_j - r_k) - \frac{1}{r^2_{jk}} \right]$$

$$\cdot s_k + \sum_{j<k} \frac{1}{c^2} \frac{1}{r^2_{jk}} s_j \cdot [r_k - r_j] \times \nabla_k$$

$$+ \sum_{j<k} \frac{1}{c^2} \frac{1}{r^2_{jk}} s_j \cdot [r_k - r_j] \times \nabla_k.$$  

(10)

The first and second terms of $V_2$ correspond to the electron–electron Darwin and retardation terms, respectively. As long as spin-unpolarized systems, such as the closed-shell atoms, are considered, the second and third lines of equation (10) vanishes.
From the point of view of the Hohenberg–Kohn theorem, the functional $F$ is used in the Schrödinger scheme for the interaction $1/r_{ij} + V^\prime_2 (r_j,r_s,s_j,s_k)$.

### 2.3. DFT with finite-light-speed correction

In order to reformulate DFT on the basis of the Hartree energy and potential corresponding to the emission of a finite-energy transfer, while the Hartree term corresponds to zero-energy transfer.

The relativist corrections of the Hartree and the exchange–correlation energy densities shown with solid and long-dashed lines, respectively, as functions of the Wigner–Seitz radius $r_s$ in figure 1. For comparison, the Non-rel LDA exchange–correlation energy density in the PZ81 functional and the total LDA exchange–correlation energy density are also shown with dashed and dash–dotted lines, respectively.

Figure 1. Relativistic corrections of the Hartree and the exchange–correlation (xc) energy densities shown with solid and long-dashed lines, respectively, as functions of the Wigner–Seitz radius $r_s$. For comparison, the Non-rel LDA exchange–correlation energy density in the PZ81 functional and the total LDA exchange–correlation energy density are also shown with dashed and dot-dashed lines, respectively.

For calculation of isolated atoms, the spherical symmetry is assumed to the effective Kohn–Sham potential $V_{KS}$, since the $V_{ext}$ has the spherical symmetry and is much stronger than the $V_{int}$. In the one-body relativistic correction $V^r_1$, the delta function is included, and this term often causes numerical instability. In order to avoid this problem, the scalar-relativistic (Scalar-rel) approximation [69]

$$\hat{h}_{KS} = -\frac{\hbar^2}{2M} \left[ \Delta_r + \frac{l(l+1)}{r^2} \right] + V_{KS} (r) - \frac{1}{4M^2c^2} \int \frac{dV_{KS}}{dr} \frac{d}{dr}$$

is applied to the single-particle Schrödinger kinetic operator and the external potential, $\hat{r}^2 + V_{ext} + V^r_1$, where $M$ is the energy-dependent effective mass

$$M = m_e + \frac{e^2 V_{KS}}{2c^2}.$$
spin–orbit interaction in electron systems is weak enough [71],

2.4. Spin–orbit interaction

$\Delta_r = \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr}$,

and $l$ is the azimuthal quantum number. With this approximation, the one-body relativistic effects $V'_l$ are included accurately. Hence, the Kohn–Sham effective potential does not include $V'_l$ explicitly as

$$V_{KS} (r) = V_{xc} (r) + \int \frac{\rho (r')}{|r-r'|} dr' + V_{\text{rel}} (r) + V_{xc} (r),$$

where $V_{xc}$ is the exchange–correlation potential.

It should be noted that if the spin–orbit interaction is added to the Scalar-rel Hamiltonian, the eigenvalues and eigenfunctions of the Hamiltonian are exactly identical to those of the original Hamiltonian, whereas the Foldy–Wouthuysen transformed Hamiltonian not [70].

2.4. Spin–orbit interaction

The spin–orbit interaction, which is ignored with the Scalar-rel approximation, is treated as follows. It is known that the spin–orbit interaction in electron systems is weak enough [71], and hence, it is treated in the first-order perturbation theory.

The spin–orbit interaction in this scheme is

$$V_{SO} (r) = -\frac{1}{4M^2c^2} \kappa + \frac{1}{r} \frac{dV_{KS} (r)}{dr}.$$  (21)
The spin–orbit interaction is given by \[ \kappa j \]

where \( j = l \pm 1/2 \) is the total angular momentum. Here, \( \kappa = + (j + 1/2) \) for \( j = l + 1/2 \) and \( \kappa = - (j + 1/2) \) for \( j = l - 1/2 \). Correction of the single-particle energy due to the first-order perturbation theory for the spin–orbit interaction is

\[
E_{\text{SO}}^{j,l} = \langle \psi_{n,l} | V_{\text{SO}} | \psi_{n,l} \rangle = \kappa + 1 \left( \frac{1}{c + (\varepsilon_{n,l} - V_{\text{KS}})/2c} \right) \int \frac{dV_{\text{KS}}(r)}{dr} |R_{n,l}(r)|^2 r dr,
\]

where \( \psi_{n,l} \) and \( \varepsilon_{n,l} \) are the Kohn–Sham single-particle orbitals and energies, respectively, and \( R_{n,l} \) is the radial part of \( \psi_{n,l} \).

3. Calculations and discussion

In this section, calculation results given by the present scheme are shown. Electronic properties of atomic systems are calculated as a benchmark. The electron density is approximated to be the spherical symmetric.

The scheme developed in this paper is called ‘SRel-CB’, which is an abbreviation of the Scalar-rel scheme with the Coulomb–Breit interaction. The results are compared with those with the Non-rel and Scalar-rel schemes without the Breit correction. Here, the Non-rel scheme means the original Schrödinger formalism. The PZ81 [49] functional is used as the exchange–correlation functional for the Non-rel and Scalar-rel schemes. The ADPACK code [81] with implementing the SRel-CB scheme is used for the calculation.

3.1. Radium

The ground-state energy of a radium (Z = 88) atom is calculated. The electronic configuration of the atom is [Rn] 7s\(^2\). Therefore, the spin–orbit interaction in the first-order perturbation theory does not affect the total ground-state energy and density.

The electronic single-particle energy of the radium atom calculated in the SRel-CB scheme with and without the spin–orbit interaction (SO) are shown in table 1. For comparison, those calculated in the Non-rel and Scalar-rel schemes are also shown.

We show in table 2 that sum of the single-particle energies \( \sum_j \varepsilon_j \), the kinetic energy \( T \), the Hartree energy \( E_{\text{H}} \), the exchange–correlation energy \( E_{\text{xc}} \), the external potential energy \( E_{\text{ext}} \), and the total energy \( E_{\text{tot}} \) calculated in the SRel-CB, Non-rel, and Scalar-rel schemes. For comparison, the ratio of each energy to that of the Non-rel scheme is also shown.

The density distribution \( \rho(r) \) calculated in the SRel-CB scheme is shown in figure 2(a) as a solid line. For comparison, those calculated in the Non-rel and Scalar-rel schemes are shown as long-dashed, dashed lines, respectively. The ratio of density distribution to that in the Non-rel is shown in figure 2(b).

First, let us see the effect of the one-body correction \( V'_{1} \) with the comparison between ‘Non-rel’ and ‘Scalar-rel’ in tables 1 and 2 and figure 2. Because \( V'_{1} \) is the attractive, it localizes the density more than that in the Non-rel scheme as shown in figure 2. Due to this localization, the external potential energy \( E_{\text{ext}} \) and the kinetic energy \( T \) are changed significantly as shown in table 2. The single-particle energies summarized in table 1 indicate that the s and p orbitals are bound more deeply due to the mass–velocity effect, while d and f orbitals are bound more shallowly in order to be orthonormal to s and p orbitals as known, e.g., in references [72–74].

Next, let us see the effect of the two-body correction \( V'_{2} \) with the comparison between ‘Scalar-rel’ and ‘SRel-CB’ in tables 1 and 2 and figure 2. The effects of \( V'_{2} \) is opposite of \( V'_{1} \). We can find in figure 2 that the density in the SRel-CB scheme is more delocalized than that in the Scalar-rel scheme. The delocalization is understood as a consequence of the cancellation of non-relativistic and relativistic contributions to the exchange–correlation energy density \( \varepsilon_{\text{xc}} \). Without \( V'_{2} \), \( \varepsilon_{\text{xc}} \) has monotonically negative values near the ionic core as shown in figure 1. The relativistic correction originating from \( V'_{2} \) partially cancels this negative value, which results in weakening of the electron attractive potential in the core region. Note that this charge delocalization has little effect on the energies \( \sum \varepsilon_j, T, E_{\text{H}}, \) and \( E_{\text{xc}} \). The change in \( E_{\text{xc}} \) is found to be mainly due to the change of the functional form. The single-particle energies summarized in table 1 indicate that the s and p orbitals are bound more shallowly. Although the effect on d and f orbitals is non-monotonic, we find a tendency that those
Table 3. Total energies for selected atoms in the SRel-CB scheme. For comparison, total energies calculated in the Non-rel and Scalar-rel schemes are also shown. All units are in the Hartree atomic unit.

| Atoms      | Z   | Non-rel | Scalar-rel | SRel-CB  |
|------------|-----|---------|------------|----------|
| Helium     | 2   | −2.834 35 | −2.834 48  | −2.834 39 |
| Lithium    | 3   | −7.334 20 | −7.334 99  | −7.334 57 |
| Beryllium  | 4   | −14.446 37| −14.449 20 | −14.448 00|
| Neon       | 10  | −128.228 11| −128.372 90| −128.346 37|
| Sodium     | 11  | −161.434 35| −161.653 67| −161.616 80|
| Magnesium  | 12  | −199.133 69| −199.454 49| −199.404 93|
| Argon      | 18  | −525.939 71| −527.808 02| −527.611 30|
| Potassium  | 19  | −598.193 57| −600.557 12| −600.320 52|
| Calcium    | 20  | −675.735 08| −678.687 69| −678.407 88|
| Krypton    | 36  | −2750.136 29| −2786.820 81| −2784.744 30|
| Rubidium   | 37  | −2936.325 53| −2977.620 68| −2975.353 56|
| Strontium  | 38  | −3129.441 31| −3175.786 66| −3173.277 51|
| Xenon      | 54  | −7228.838 84| −7441.147 22| −7432.271 64|
| Caesium    | 55  | −7550.540 03| −7780.593 33| −7771.086 92|
| Barium     | 56  | −7880.093 28| −8129.043 11| −8118.868 79|
| Radon      | 86  | −21861.294 05| −23538.401 47| −23477.933 63|
| Francium   | 87  | −22470.265 26| −24239.483 11| −24175.506 69|
| Radium     | 88  | −23088.631 12| −24954.194 43| −24886.500 50|

![Graph](image1.png)  
**Figure 3.** Ratio of the energies calculated in the SRel-CB scheme to those in the Non-rel one. The Hartree energy $E_{\text{H}}$, exchange–correlation energy $E_{\text{xc}}$, and energy from the one-body term $T_0 + E_{\text{ext}}$ are shown in solid, long-dashed, and dash-dotted lines, respectively.

![Graph](image2.png)  
**Figure 4.** Same as figure 3 but compared with the Scalar-rel scheme. Since the one-body operator in this work is the same as that in the Scalar-rel calculation, energy from the one-body term $T_0 + E_{\text{ext}}$ is not shown.

with large principal quantum numbers bound more deeply. Since the exchange–correlation energy contributes to the total energy less than 10%, even though that in the SRel-CB scheme is changed drastically from those in the other relativistic calculations, the density distribution in this work is almost the same. More detailed discussion will be given in the next subsection.

The spin–orbit interaction affects all the orbitals except the $s$ orbitals. Since its strength is often wholly comparable to $V_1$, once we incorporate this, the view on the $V_1$ effects on the single-particle energies does not straightforwardly apply to the individual spin–orbit partners. Note that the above discussion on $V_1$ is still valid as seen from columns ‘Scalar-rel + SO’ and ‘SRel-CB + SO’.

In short, the $s$ and $p$ orbitals are bound more deeply due to $V_1$, and more shallowly due to $V_2$. In total, they are bound more deeply since the effect of $V_1$ is larger than that of $V_2$. The $d$ and $f$ orbitals tend to show opposite behavior from the $s$ and $p$ orbitals.

3.2. Groups 1, 2, and 18 elements

In order to discuss the systematic behavior of relativistic effects in this scheme, properties of all the groups 1, 2, and 18 atoms are calculated. We do not address the hydrogen atom since it has only one electron, and therefore, the exchange–correlation term is zero. All the group 18 atoms are closed shell and all the group 1 and 2 atoms are closed-shell plus $s$ electrons. Therefore, the spin–orbit interaction does not affect the total energies in these atoms in the first-order perturbation theory.
The total energies calculated in the Non-rel, Scalar-rel, and SRel-CB schemes are shown in Table 3. It is seen that the relativistic effects of $V'_2$ are non-negligible in heavier atoms as well as those of $V'_1$, and the former effects for the total energy are opposite to the latter.

We here analyze the contributions of the Hartree $E_H$ and exchange–correlation $E_{xc}$ energies and energy from the one-body term $T_0 + E_{ext}$ separately. The ratios of these values in the SRel-CB scheme, $E_{SRel-CB}$, to those in the Non-rel scheme, $E_{Non-rel}$, are shown in figure 3, and ratios to those in the Scalar-rel, $E_{Scalar-rel}$, are shown in figure 4. Those for the Hartree energy $E_H$, exchange–correlation energy $E_{xc}$, and energy from the one-body term $T_0 + E_{ext}$ are shown in solid, long-dashed, and dash-dotted lines, respectively. Since the one-body operator in the SRel-CB scheme is the same as that in the Scalar-rel scheme, the ratio of the one-body term $T_0 + E_{ext}$ is not shown.

The relativistic correction to the external potential $V'_1$, which is the attractive force, makes the external attractive potential stronger, whereas that to the interaction $V'_2$, which is also the attractive force, makes the repulsive interaction smaller. Thus, the relativistic effects make the energy due to the potential, $E_{ext}$, larger, while that makes the energies due to the interaction, $E_H$ and $E_{xc}$, weaker, as shown in figure 3. However, a lot of effects, such as the change of the Kohn–Sham orbitals, are entangled to each other in the self-consistent step, and eventually $E_H$ in the SRel-CB scheme is larger than that in the Non-rel scheme.

Between $E_H$ and $E_{xc}$, $E_{SRel-CB}/E_{Scalar-rel}$ for $E_H$ is smaller than $E_{xc}$. The interaction includes the finite-light-speed effect as well as effects coming from the Dirac equation, whereas the finite-light-speed effect of the Hartree term vanishes. As a result, the relativistic correction of the Hartree energy is smaller than that of the exchange–correlation energy, as also discussed in section 2.3. Since the absolute value of the Non-rel Hartree term is larger than that of the Non-rel exchange–correlation term, finally, the ratios $E_{Scalar-rel}/E_{Non-rel}$ and $E_{SRel-CB}/E_{Non-rel}$ of the Hartree energy are further smaller than those of the exchange–correlation energy as shown in figure 4. Therefore, it can be concluded that the finite-light-speed correction is less significant than effects coming from the Dirac equation for the electron–electron interaction.

One can also find that the relativistic corrections are more significant in larger Z. According to figure 1, the relativistic corrections are significant in $r_s \lesssim 0.1$ a.u. region. As $Z$ increases, the density also increases, and notably, the region with $r_s \lesssim 0.1$ a.u. extends. In consequence, the relativistic effects in larger $Z$ are more significant, as shown in figures 3 and 4.

### 3.3. Lawrencium and lutetium

We compare the energies of two cases of the electronic configuration of lawrencium atoms, where one valence electron occupies the 6d orbital ([$\text{Rn}$] 5f⁰ 6d¹ 7s¹) or occupies the 7p orbital ([$\text{Rn}$] 5f⁰ 7s¹ 7p¹). For comparison, those of lutetium atoms are also calculated, where one valence electron occupies the 5d orbital ([$\text{Xe}$] 4f⁰ 5d¹ 6s²) or occupies the 6p orbital ([$\text{Xe}$] 4f⁰ 5d² 6p¹). The non-spherical modification in $V_{KS}$ is ignored for simplicity. In principle, both the lutetium and lawrencium are open-shell atoms, and thus the effective potential $V_{KS}$ may be non-spherical. Since there is strong spherical (central) external potential caused by the atomic nucleus, it is assumed that the single-particle energies and total energies are scarcely affected by the non-sphericity of $V_{KS}$.

The energies calculated with the above-mentioned configuration are shown in table 4. All energies are calculated in the Non-rel, Scalar-rel, and SRel-CB schemes. The smaller values for the respective approximations in each atom are shown with the bold font.

On the one hand, in lutetium atoms, the electron prefers to occupy the $d$ orbital rather than the $p$ orbital in all schemes. On the other hand, in lawrencium atoms, the electron prefers to occupy the $p$ orbital rather than the $d$ orbital in the SRel-CB scheme, whereas it still prefers the $d$ orbital in the Non-rel scheme like the lutetium case. In addition, the electron is unbound for lawrencium atoms in the Scalar-rel scheme. We can understand the dependence of the electronic configuration in lawrencium atoms on the level of the approximation with the single-particle orbitals discussed in section 3.1. Due to the relativistic corrections $V'_1$ and $V'_2$, the 6d orbital may be bound shallower, while the 7p orbital may be bound deeper, compared with the results in the Non-rel scheme. As a result, the 6d orbital may become unbound, while the 7p orbital is still kept bound.

The present results suggest that a valence electron occupies $p$ orbitals in lawrencium atoms, where the finite-light-speed correction to the Coulomb interaction has a crucial role. The occupation of $p$ orbital could be the origin of the anomalous behavior of the lawrencium [7, 8].

### 4. Conclusion

In this paper, a non-relativistic-reduction-based approach to the LDA for DFT with the relativistic correction up to
Hamiltonian is the same as the case of Non-relLDA. The way to construct DFT scheme from the wave-function methods to discuss the electronic structure in this paper is the same as the Hamiltonian previously used in the paper the Hartree term with the Breit correction is derived, while the term vanishes in the spin-unpolarized systems. This effect has never been considered and this may give rise to non-trivial phenomena. Also, the Hartree energy due to the retardation term $V_z$, which is zero in the time-reversal symmetric case, can be nonzero. In order to consider these effects in the calculation of solids, construction of the pseudopotential is also required [53].

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Appendix A. Two relativistic correction for the exchange–correlation functionals

The LDA form derived by Kenny et al [42] is used in this paper to consider the Breit correction for the exchange–correlation functional $E_{xc}$. This form has been constructed in the same way as the non-relativistic LDA exchange–correlation functional, PZ81 [49], while the Coulomb–Breit interaction is used for the electron–electron interaction $V_{\text{int}}$ instead of the Coulomb interaction. There is another relativistic correction for the exchange functional in LDA derived by McDonald and Vosko [40]. This functional is constructed in the same way as the non-relativistic LDA exchange functional, i.e., the Hartree–Fock–Slater approximation as

$$
\varepsilon_x (\rho) = -\frac{3}{4} \left(3 \frac{\pi}{\rho}\right)^{1/3} \left[1 - \frac{2}{3} \left(\frac{3\pi^2 \rho}{c^2}\right)^{2/3}\right].
$$

(A.1)

The relativistic correction to the correlation part is not considered in this functional. In this appendix, the above-mentioned two relativistic corrections for $E_{xc}$ are discussed. The relativistic corrections derived by Kenny et al [42] and by MacDonald and Vosko [40] are referred to as ‘LDA-RK’ and ‘LDA-RMV’, respectively.

In table A1, the total energies calculated in the non-relativistic and relativistic LDA exchange–correlation functional are shown, where the PZ81 functional is used for the
non-relativistic functional, while the LDA-RK and LDA-RMV functionals are used for the relativistic functional. For comparison, the result with the Non-rel GGA exchange–correlation functional is also shown, where the PBE functional [55] is used. For the kinetic term and the Hartree term, the Non-rel scheme is used.

In this section, the derivation of $E_{\text{Hrel}}$ (equation (16)) is appended. We define the contribution from the first and second terms of $V_{\text{5}}$ as $E_{\text{H1}}$ and $E_{\text{H2}}$, respectively, as $E_{\text{Hrel}} = E_{\text{H1}} + E_{\text{H2}}$:

$$E_{\text{H1}} [\rho] = - \frac{\pi}{252} \sum_{j \neq k} \int \int \psi_j^*(r) \psi_k^*(r') d^3r \delta (r-r') \int \int \psi_j(r) \psi_k(r') d^3r'$$

$$E_{\text{H2}} [\rho] = - \frac{1}{4\pi c^2} \sum_{j \neq k} \int \int \psi_j^*(r) \psi_k^*(r') \left[ \frac{(r-r') \cdot (r-r')}{|r-r'|^3} + \frac{1}{|r-r'|} \right] \nabla \psi_j (r) \psi_k (r') d^3r d^3r'$$

### Appendix B. Relativistic correction of Hartree term

In this section, the derivation of $E_{\text{Hrel}}$ (equation (16)) is appended. We define the contribution from the first and second terms of $V_{\text{5}}$ as $E_{\text{H1}}$ and $E_{\text{H2}}$, respectively, as $E_{\text{Hrel}} = E_{\text{H1}} + E_{\text{H2}}$:

$$E_{\text{H1}} [\rho] = - \frac{\pi}{252} \sum_{j \neq k} \int \int \psi_j^*(r) \psi_k^*(r') d^3r \delta (r-r') \int \int \psi_j(r) \psi_k(r') d^3r'$$

$$E_{\text{H2}} [\rho] = - \frac{1}{4\pi c^2} \sum_{j \neq k} \int \int \psi_j^*(r) \psi_k^*(r') \left[ \frac{(r-r') \cdot (r-r')}{|r-r'|^3} + \frac{1}{|r-r'|} \right] \nabla \psi_j (r) \psi_k (r') d^3r d^3r'$$

### Table A1. Total energies calculated in the non-relativistic and relativistic LDA exchange–correlation functionals. For the non-relativistic functional, the PZ81 functional is used, while for the relativistic functional, the LDA-RK and the LDA-RMV functionals are used. For comparison, the Non-rel GGA exchange–correlation functional is also shown, where the PBE functional [55] is used. For the kinetic term and the Hartree term, the Non-rel scheme is used.

| Atoms       | $Z$ | PZ81   | PBE   | LDA-RK | LDA-RMV |
|-------------|-----|--------|-------|--------|---------|
| Helium      | 2   | −2.83435 | −2.89288 | −2.83419 | −2.83417 |
| Lithium     | 3   | −7.33420 | −7.45114 | −7.33353 | −7.33345 |
| Beryllium   | 4   | −14.44637 | −14.62934 | −14.44430 | −14.44433 |
| Neon        | 10  | −128.22811 | −128.85570 | −128.18769 | −128.18595 |
| Sodium      | 11  | −161.43435 | −162.15032 | −161.37830 | −161.37630 |
| Magnesium   | 12  | −199.13369 | −199.93645 | −199.05876 | −199.05601 |
| Argon       | 18  | −525.93971 | −527.28209 | −525.64756 | −525.63985 |
| Potassium   | 19  | −598.19357 | −599.62967 | −597.84352 | −597.83468 |
| Calcium     | 20  | −675.73508 | −677.26086 | −675.31933 | −675.30929 |
| Krypton     | 36  | −2750.13629 | −2752.92551 | −2747.28274 | −2747.23853 |
| Rubidium    | 37  | −2936.32553 | −2939.18962 | −2933.20263 | −2933.15523 |
| Strontium   | 38  | −3129.44131 | −3132.37553 | −3126.03205 | −3125.98133 |
| Xenon       | 54  | −7228.83884 | −7232.68662 | −7218.08285 | −7217.95898 |
| Caesium     | 55  | −7550.54003 | −7554.42904 | −7539.11954 | −7538.98974 |
| Barium      | 56  | −7880.09328 | −7884.01939 | −7867.98002 | −7867.84414 |
| Radon       | 86  | −21861.29405 | −21865.09427 | −21812.86582 | −21812.45816 |
| Francium    | 87  | −22470.26526 | −22474.02687 | −22419.98747 | −22419.56745 |
| Radium      | 88  | −23088.63112 | −23092.34870 | −23036.45668 | −23036.02407 |

![Figure A1. Ratio of the total energy calculated with the LDA-RK, LDA-RMV, and PBE functionals to that calculated with the PZ81, $\Delta E_{\text{tot}}$ shown in solid, dashed, and dash-dotted lines, respectively.](image)
where the summation runs over the occupied states only. The $j = k$ contribution can be included in equations (B.1) and (B.2) since they are canceled by the exchange terms, and thus $\sum_{j \neq k}$ can be replaced to $\sum_{jk}$. Here, we derive the density functional forms of $E_{\text{H1}}$ and $E_{\text{H2}}$.

The first term $E_{\text{H1}}$ is straightforwardly transformed as

$$
E_{\text{H1}} [\rho] = -\frac{\pi}{2e^2} \sum_{j \in \text{occ}} \int \int \psi_j^* (r) \psi_k^* (r') \delta (r - r') \psi_j (r) \psi_k (r') dr dr' = -\frac{\pi}{2e^2} \sum_{j \in \text{occ}} \frac{|\rho (r)|^2}{\rho (r)} dr.
$$

(B.3)

Next, relativistic correction $E_{\text{H2}}$ is derived with the assumption that the system has the time-reversal symmetry. Here, the density is written with the single-particle Kohn–Sham orbital as

$$
\rho (r) = \sum_{j \in \text{occ}} c_j \psi_j^* (r) \psi_j (r).
$$

(B.4)

The time-reversal symmetry ensures that any complex conjugate of the occupied eigenstate is also occupied eigenstate and here its index is denoted as $j^*$ with $\psi_j^* = \psi_{j^*}$. Thus, the component

$$
\sum_{j \in \text{occ}} \left[ \nabla \psi_j^* (r) \psi_j (r) \right]
$$

can be written as

$$
\sum_{j \in \text{occ}} \left[ \nabla \psi_j^* (r) \psi_j (r) \right] = \frac{1}{2} \sum_{j \in \text{occ}} \left[ \nabla \psi_j^* (r) \psi_j (r) + \nabla \psi_j^* (r) \psi_j^* (r) \right] = \frac{1}{2} \nabla \sum_{j \in \text{occ}} \psi_j^* (r)^2 = \frac{1}{2} \nabla \rho (r).
$$

Equation (B.2), hence, reads

$$
E_{\text{H2}} [\rho] = -\frac{1}{4e^2} \sum_{j \in \text{occ}} \int \int \psi_j^* (r) \psi_j^* (r') \left[ \frac{(r - r') \cdot (r - r')}{|r - r'|^3} + \frac{1}{|r - r'|} \right] \psi_j (r) \psi_j (r') dr dr'
$$

$$
= \frac{1}{4e^2} \sum_{j \in \text{occ}} \int \int \psi_j^* (r) \left[ \frac{(r - r') \cdot \nabla \psi_j (r)}{|r - r'|^3} \right] \psi_j (r) dr dr' - \frac{1}{4e^2} \sum_{j \in \text{occ}} \int \int \psi_j^* (r) \left[ \frac{\nabla \psi_j (r) \cdot \nabla \psi_j (r)}{|r - r'|} \right] \psi_j (r) dr dr' 
$$

$$
= \frac{1}{16e^2} \sum_{j \in \text{occ}} \int \left[ \frac{(r - r') \cdot \nabla \rho (r)}{|r - r'|^3} \right] \frac{(r - r') \cdot \nabla \rho (r')}{|r - r'|^3} dr dr' + \frac{(\nabla \rho (r)) \cdot (\nabla \rho (r'))}{|r - r'|^3} dr dr'.
$$

(B.6)

Here, in the atomic systems, the density $\rho$ satisfies $\rho (r) \to 0$ in $r \to \infty$. Under this assumption, since

$$
\frac{\partial}{\partial r} \frac{1}{|r - r'|^3} = -\frac{r_j - r'_j}{|r - r'|^3} (j = x, y, z),
$$

(B.7)

the second term of equation (B.6) reads

$$
\int \int \left\{ \nabla \rho (r) \cdot \nabla \rho (r') \right\} \frac{dr \, dr'}{|r - r'|^3} = -\int \rho (r) \nabla \frac{\nabla \rho (r)}{|r - r'|^3} dr \, dr' = \int \rho (r) \left( \frac{r - r'}{|r - r'|^3} \right) \frac{\partial \rho (r)}{|r - r'|^3} dr \, dr'.
$$

(B.8)

Since

$$
\frac{\partial}{\partial r} \left( \frac{r_j - r'_j}{|r - r'|^3} \right) = \frac{r_j - r'_j}{|r - r'|^3} + \frac{r_j - r'_j}{|r - r'|^3} \delta_{jj} - 3 \frac{(r_j - r'_j)^2 (r_j - r'_j)}{|r - r'|^5}
$$

(B.9)

and

$$
\sum_{i,j=1}^3 \frac{\partial}{\partial r} \left( \frac{r_j - r'_j}{|r - r'|^3} \right) \frac{\partial^2 \rho (r)}{|r - r'|^3} = \sum_{i,j=1}^3 \frac{r_j - r'_j}{|r - r'|^3} \frac{\partial^2 \rho (r)}{|r - r'|^3} + \sum_{i=1}^3 \frac{r_i - r'_i}{|r - r'|^3} \frac{\partial^2 \rho (r)}{|r - r'|^3}
$$

$$
- 3 \sum_{i,j=1}^3 \frac{(r_j - r'_j)^2 (r_j - r'_j)}{|r - r'|^3} \frac{\partial^2 \rho (r)}{|r - r'|^3} = \frac{4 (r - r') \cdot \nabla \rho (r)}{|r - r'|^3} + \sum_{i=1}^3 \frac{r_i - r'_i}{|r - r'|^3} \frac{\partial \rho (r)}{|r - r'|^3}
$$

$$
- 3 \sum_{i,j=1}^3 \frac{(r_i - r_j)^2 (r_i - r_j)}{|r - r'|^3} \frac{\partial^2 \rho (r)}{|r - r'|^3} = \frac{\nabla \rho (r)}{|r - r'|^3},
$$

(B.10)

the first term of equation (B.6) reads

$$
\int \int \left. \left\{ \frac{(r - r') \cdot \nabla \rho (r)}{|r - r'|^3} \right\} \frac{dr \, dr'}{|r - r'|^3} = \int \sum_{i,j=1}^3 \frac{(r_i - r'_j) \partial \rho (r)}{|r - r'|^3} \left( \frac{(r_j - r'_j) \partial \rho (r)}{|r - r'|^3} \right) dr \, dr' = \int \sum_{i,j=1}^3 \frac{(r_i - r'_j) (r_j - r'_j) \partial \rho (r) \partial \rho (r)}{|r - r'|^3} dr \, dr'.
$$
Therefore, equation (B.6) reads

\[ \rho \left( \mathbf{r} \right) \cdot \left( 1 - \frac{1}{4} \mathbf{r} \cdot \nabla \rho \left( \mathbf{r} \right) \right) \]

(\text{B.6})

Finally,

\[ E_{\text{HII}} \left[ \rho \right] = \frac{1}{2} \int \rho \left( \mathbf{r} \right) \mathbf{r} \cdot \left( \mathbf{r} \right) \, d\mathbf{r} \]

(\text{B.13})

is followed.

References

[1] Mingos D M P (ed) 2019 *The Periodic Table I (Structure and Bonding* vol 181) (Berlin: Springer)
[2] Morita K et al 2004 *J. Phys. Soc. Japan* 73 2593
[3] Oganessian Y T et al 2004 *Phys. Rev. C* 69 021601
[4] Oganessian Y T et al 2013 *Phys. Rev. C* 87 054621
[5] Khuyagbaatar J et al 2014 *Phys. Rev. Lett.* 112 172501
[6] Oganessian Y T et al 2006 *Phys. Rev. C* 74 044602
[7] Sato T K et al 2015 *Nature* 520 209
[8] IUPAC Bureau Members 2015 48th IUPAC Council Meeting Final Agenda Book (Research Triangle, NC: IUPAC)
[9] Pykkoj P 2011 *Phys. Chem. Chem. Phys.* 13 161
[10] Eides M I, Grotch H and Shellyuto V A 2001 *Phys. Rep.* 342 63
[11] Schädel M 2006 *Angew. Chem., Int. Ed.* 45 368
[12] Schädel M and Shaughnessy D (eds) 2014 *The Chemistry of Superheavy Elements* (Berlin: Springer)
[13] Weinberg S 1995 *The Quantum Theory of Fields* (Cambridge: Cambridge University Press)
[14] Breit G 1929 *Phys. Rev.* 34 553
[15] Breit G 1930 *Phys. Rev.* 36 383
[16] Hohenberg P and Kohn W 1964 *Phys. Rev.* 136 B864
[17] Kohn W and Sham L J 1965 *Phys. Rev.* 140 A1133
[18] Kohn W 1999 *Rev. Mod. Phys.* 71 1253
[19] Eliav E, Kaldor U and Ishikawa Y 1995 *Phys. Rev. A* 52 291
[20] Borschevsky A, Eliav E, Vilkas M J, Ishikawa Y and Kaldor U 2007 *Eur. Phys. J. D* 45 115
[21] Sahoo B K, Nandy D K, Das B P and Sakemi Y 2015 *Phys. Rev. A* 91 042507
[22] Borschevsky A, Pašteka L F, Pershina V, Eliav E and Kaldor U 2015 *Phys. Rev. A* 91 020501
[23] Eliav E, Fritzschke S and Kaldor U 2015 *Nucl. Phys. A* 944 518
[24] Pershina V 2015 *Nucl. Phys. A* 944 578
[25] Sahoo B K, Aoki T, Das B P and Sakemi Y 2016 *Phys. Rev. A* 93 032520
[26] Desclaux J P and Fricke B 1980 *J. Phys. A* 13 943
[27] Cao X, Dolg M and Stoll H 2003 *J. Chem. Phys.* 118 487
[28] Polle J A, Binkley J S and Seeger R 1976 *Int. J. Quantum Chem.* 10 1
[29] Polle J A, Seeger R and Krishman R 1977 *Int. J. Quantum Chem.* 12 149
[30] Polle J A 1999 *Rev. Mod. Phys.* 71 1267
[31] Coester F 1958 *Nucl. Phys.* 74 337
[32] Žúžek J and Paldus J 1971 *Int. J. Quantum Chem.* 5 359
[33] Jensen F 2017 *Introduction to Computational Chemistry* 3rd edn (New York: Wiley)
[34] Evarestov R A 2012 *Quantum Chemistry of Solids (Springer Series in Solid-State Sciences* vol 153) 2nd edn (Berlin: Springer)
[35] Nagami Y, Kratz J V and Schädel M 2015 *Nucl. Phys. A* 944 614
[36] Türlar A, Eichler R and Yakushev A 2015 *Nucl. Phys. A* 944 640
[37] Rajagopal A K and Callaway J 1973 *Phys. Rev. B* 7 1912
[38] Rajagopal A K 1978 *J. Phys. C* 11 L943
[39] MacDonald A H and Vosko S H 1979 *J. Phys. C* 12 2977
[40] Engel E 2002 *Relativistic density functional theory: foundations and basic formalism relativistic electronic structure theory Handbook of Relativistic Quantum Chemistry (Theoretical and Computational Chemistry* vol 11) ed P Schwerdtfeger (Amsterdam: Elsevier) pp 547–78 ch 10
[41] Kenny S D, Rajagopal G, Needs R J, Leung W K, Godfrey M J, Williamson A J and Foulkes W M C 1996 *Phys. Rev. Lett.* 77 1099
[42] Engel E, Keller S and Dreizler R M 1996 *Phys. Rev. A* 53 1367
[43] Engel E, Facco Bonetti A, Keller S, Andrejkoivcs I and Dreizler R M 1998 *Phys. Rev. A* 58 964
[44] Kreibich T, Gross E K U and Engel E 1998 *Phys. Rev. A* 57 138
[45] Filatov M and Cremer D 2002 *Chem. Phys. Lett.* 351 259
[46] Liu W, Küchle W and Dold M 1998 *Phys. Rev. A* 58 1103
[47] Bornemann S, Minár J, Braun J, Köderitzsch D and Ebert H 2012 *Solid State Commun.* 152 85
[48] Perdew J P and Zunger A 1981 *Phys. Rev. B* 23 1625
[49] Vosko S H, Lavigo J B and Mayer I L 1980 *Phys. Rev. A* 23 2593
[50] Lagowski J B and Vosko S H 1989 *Phys. Rev. A* 39 4972
[51] Vukajlovic F R, Shirley E L and Martin R M 1991 *Phys. Rev. B* 43 3994
[52] Martin R M 2004 *Electronic Structure* (Cambridge: Cambridge University Press)
[53] Kosugi T, Nishi H, Furukawa Y and Matsushita Y i 2018 *J. Chem. Phys.* 148 224103
[54] Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* 77 3865
[55] Engel E and Dreizler R M 2011 *Density Functional Theory—An Advanced Course Theoretical and Mathematical Physics* (Berlin: Springer)
[56] Perdew J P, Parr R G, Levy M and Balduz J L 1982 *Phys. Rev. Lett.* 49 1691
[57] Engel E, Chevary J A, MacDonald L D and Vosko S H 1992 *Z. Phys. D* 23 7
[58] Vydrov O A, Scuseria G E and Perdew J P 2007 *J. Chem. Phys.* 126 154109
[60] Fiolhais C, Nogueira F and Marques M A L (eds) 2003 A Primer in Density Functional Theory (Lecture Notes in Physics vol 620) (Berlin: Springer)

[61] Perdew J 1979 Chem. Phys. Lett. 64 127

[62] Zhang Y and Yang W 1998 J. Chem. Phys. 109 2604

[63] Perdew J P, Constantin L A, Sagvolden E and Burke K 2006 Phys. Rev. Lett. 97 223002

[64] Pryce M H L 1948 Proc. R. Soc. A 195 62

[65] Foldy L L and Wouthuysen S A 1950 Phys. Rev. 78 29

[66] Tani S 1951 Prog. Theor. Phys. 6 267

[67] Foldy L L 1952 Phys. Rev. 87 688

[68] Kenny S D, Rajagopal G and Needs R J 1995 Phys. Rev. A 51 1898

[69] Koelling D D and Harmon B N 1977 J. Phys. C 10 3107

[70] Liang H, Meng J and Zhou S G 2015 Phys. Rep. 570 1

[71] Saue T 2011 ChemPhysChem 12 3077

[72] Rose S J, Grant I P and Pyper N C 1978 J. Phys. B 11 1171

[73] Pyykö P 1988 Chem. Rev. 88 563

[74] Bartlett N 1998 Gold Bull. 31 22

[75] Cotton F A, Wilkinson G and Gauss P L 1995 Basic Inorganic Chemistry (New York: Wiley)

[76] Indelicato P, Santos J P, Boucard S and Desclaux J P 2007 Eur. Phys. J. D 45 155

[77] Indelicato P 2013 Phys. Rev. A 87 022501

[78] Pospelov M and Ritz A 2005 Ann. Phys., NY 318 119

[79] Yamanaka N, Sahoo B K, Yoshinaga N, Sato T, Asahi K and Das B P 2017 Eur. Phys. J. A 53 54

[80] Ozaki T, Kino H, Kawai H and Toyoda M 2011 ADPACK Ver.2.2 http://openmx-square.org/adpack_man2.2/