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Solving the Self-Interaction Problem in Kohn-Sham Density Functional Theory: Application to Atoms

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Abstract

In previous work, we proposed a computational methodology that addresses the elimination of the self-interaction error from the Kohn-Sham formulation of density functional theory. We demonstrated how the exchange potential can be obtained, and presented results of calculations for atomic systems up to Kr carried out within a Cartesian coordinate system. In this paper, we provide complete details of this self-interaction free method formulated in spherical coordinates based on the explicit equidensity basis ansatz. We prove analytically that derivatives obtained using this method satisfy the Virial theorem for spherical orbitals, where the problem can be reduced to one dimension. We present the results of calculations of ground-state energies of atomic systems throughout the periodic table carried out within the exchange-only mode.

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1. Introduction

The self-interaction (SI) error has been present in quantum mechanical calculations of electronic states of matter since the inception of quantum mechanics. It arises through the use of the Hartree term to approximate the electrostatic energy of a cloud of electronic charges by a density. The product of densities, as used in the Hartree term, allows the interaction of two electrons in the same single particle state (or of an electron simultaneously in two different states), that is in clear violation of the Pauli exclusion principal. The SI error was first pointed out by Fock [1] in the 1030's, when even Fermi weighed in with a suggestion for a solution [2]. The problem remained more-or-less dormant until the introduction of density functional theory (DFT) [3] in 1964 and its Kohn-Sham formulation [4] the following year, from which point the realization of its damaging effects has mushroomed, and so have the efforts at its alleviation [5].

At the same time, the computational simplicity of the Kohn-Sham method and the overall good agreement with experiment has resulted in an explosion of implementations. It was conjectured that the agreement resulted because of the cancellation of errors between the Hartree term and the so-called exchange correlation term (see below). Unfortunately, however, it was soon realized that the method failed in describing systems in which the effects of correlation (Coulomb interaction) are judged to be strong, such as semiconductors and wide-gap insulators. The method was also found to fail in describing physical effects such as binding energies, activation barriers and rates in catalytic materials, and many others. For a recent review of these problems and the generally unsatisfactory nature of various formal schemes introduced for their alleviation, of which the list included in [5] provides but a small sample, the reader is directed to the literature [6].

A method proposed recently [7, 8] addresses the SI problem for the non-interacting system in Kohn-Sham density functional theory in computationally unexpected simple fashion, using the explicit equidensity basis (EEB) ansatz.

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We define its solution as the term is used in our work: To solve the self-interaction problem one must show that the Coulomb energy is calculated in terms of the pair density, and that the Coulomb potential is obtained by functional differentiation of the Coulomb energy with respect to the density. The formalism is founded on the expansion of the Slater determinant obtained in the Kohn-Sham formalism in terms of an orthonormal and complete basis, the equidensity basis, that exhibits explicitly the density, $n(\mathbf{r})$. The advantages provided by this feature are set forth in the papers just referred to. In these papers, the equidensity basis was expressed in a Cartesian coordinate system and a corresponding grid used to store the orbitals and their spatial derivatives along with those of the density. In order to complete the algebraic aspects of the formalism we repeat key parts of the derivation in terms of a spherical coordinate system. This formulation can be used advantageously in electronic structure codes based on atom-centered coordinate systems, e.g., in linear muffin-tin orbital (LMTO) or Korringa-Kohn-Rostoker (KKR) methods. For systems where all orbitals are spherical (s-orbitals), we prove analytically that the obtained potential using the explicit equidensity ansatz satisfies the Virial theorem.

2. Theory

2.1. Conventional Kohn-Sham Theory

The solution, $\Psi(\mathbf{r}_{(N)})$, of the many-body Schrödinger equation for a quantum system of N interacting electrons under an external potential, $v(\mathbf{r})$, depends on all coordinates and is therefore hard to solve. The Kohn-Sham system [4] got introduced in conjunction with density functional theory [3] as a fictitious system of non-interacting particles which yields the same density as the original problem for the ground state. In the traditional Kohn-Sham theory the energy as a functional of the density, $n(\mathbf{r})$, is given by the expression,

$$E[n] = \int v(\mathbf{r})n(\mathbf{r})d\mathbf{r} + T_s[n] + U_H[n] + E_{xc}[n]. \quad (1)$$

$E_{xc}[n]$ denotes the exchange-correlation functional. The kinetic energy of a system of non-interacting particles is given by (the subscript s marks the non-interacting system),

$$T_s[n] = \langle \Phi | \hat{T}^N | \Phi \rangle, \quad (2)$$

where $\Phi(\mathbf{r}_1, \dots, \mathbf{r}_N) = \Phi(\mathbf{r}_{(N)})$ is a single Slater determinant constructed out of the N lowest in energy solutions, $f_j(\mathbf{r})$, of the Kohn-Sham equations,

$$\left[-\frac{1}{2}\nabla_{\mathbf{r}}^2 + v_{KS}(\mathbf{r}) \right] f_j(\mathbf{r}) = \epsilon_j f_j(\mathbf{r}), \quad (3)$$

and

$$U_H = \frac{1}{2} \int \int \frac{n(\mathbf{r}_1)n(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2, \quad (4)$$

is the Hartree energy, a classical expression for the Coulomb energy. The density given by the expression,

$$n(\mathbf{r}_1) = \int |\Phi(\mathbf{r}_{(N)})|^2 d\mathbf{r}_2 \dots d\mathbf{r}_N = \sum_{j=1}^N |f_j(\mathbf{r}_1)|^2. \quad (5)$$

The ground state of the system is determined through the minimizing of the the total energyfunctional (1). As shown by Hohenberg and Kohn [3], the basic variable of density functional theory is the density, and the condition for the ground state is that the energy be stationary with respect to changes in the density, $\frac{\delta E[n]}{\delta n} = 0$. From that condition and $\frac{\delta T_s}{\delta n} = -v_{KS}$, the Kohn-Sham potential appearing in Eq. (3) must satisfy,

$$v_{KS}(\mathbf{r}) = v(\mathbf{r}) + \frac{\delta U_H[n]}{\delta n(\mathbf{r})} + \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}. \quad (6)$$

As already pointed out in the original paper of Hohenberg and Kohn [3], the classical expression, $U_H[n]$, for the Coulomb energy was used out of convenience, allowing a simple and efficient way of performing the functional derivative of the Coulomb energy with respect to the density. The simplicity, however, comes with a steep price: As

shown above, the use of this term introduces self-interaction effects, the unphysical interaction of an electron with itself.

When the density in (5) is used in the Hartree term, it produces in the numerator inside the integral terms of the kind, $f_j(\mathbf{r}_1)f_j(\mathbf{r}_2)$, describing the interaction of two particles in the same state. The use of the Hartree term with respect to a single-electron system clearly shows the SI problem, namely, a particle in a given state interacting with itself in that state, that is in practice not compensated by the exchange correlation functional, which was defined to cancel the SI error exactly. However, this functional is unknown and in practice replaced by some approximate expression. Numerous implementations with respect to various approximate schemes for $E_{xc}[n]$ have helped reveal the true state of affairs: Approximate expressions can be designed to yield acceptable approximations to known results in a case-by-case basis, even in broad classes of systems and properties, but none can be shown *a priori* to satisfy the fundamental requirement of the Second Hohenberg-Kohn Theorem, namely that any approximate handling of the energy functional should yield an upper bound to the exact value of the ground state energy within the full solution of the corresponding Schrödinger equation. For example, the use of a given exchange-correlation functional within Kohn-Sham DFT could lead to a lower energy compared to the ground state energy of the many body solution of the equivalent Hamiltonian of the theory, were the Kohn-Sham formalism is not used.

2.2. Reformulation of the Kohn-Sham Equations

The quantum mechanically correct expression of the Coulomb energy is expressed in terms of the pair density, $n(\mathbf{r}_1, \mathbf{r}_2)$, rather than the product of densities,

$$U^{\text{QM}} = \int \int \frac{n(\mathbf{r}_1, \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2, \quad (7)$$

where the pair density can be obtained by integrating the antisymmetric, N -particle wave function, $\Psi(\mathbf{r}_{(N)})$, over all coordinates but two,

$$n(\mathbf{r}_1, \mathbf{r}_2) = \frac{N(N-1)}{2} \int |\Psi(\mathbf{r}_{(N)})|^2 d\mathbf{r}_3 \dots d\mathbf{r}_N. \quad (8)$$

Clearly, the corresponding Coulomb energy is self-interaction free. For the Kohn-Sham system, described by a single Slater determinant, the non-interacting pair density (denoted by the subscript s), is given by the expression,

$$n_s(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{4} \sum_{i,j} \delta_{\sigma_i, \sigma_j} \left| f_i^{\sigma_i}(\mathbf{r}_1) f_j^{\sigma_j}(\mathbf{r}_2) - f_j^{\sigma_j}(\mathbf{r}_1) f_i^{\sigma_i}(\mathbf{r}_2) \right|^2, \quad (9)$$

where the $f_i^{\sigma_i}(\mathbf{r})$ are the occupied states or orbitals that are the N lowest in energy solutions of the Kohn-Sham equations, and σ_i is the spin index of that particular orbital. The non-interacting pair density can be split into two parts, the contribution to the classical Hartree term, and the exchange part, J_s ,

$$n_s(\mathbf{r}_1, \mathbf{r}_2) = \frac{n(\mathbf{r}_1)n(\mathbf{r}_2) + J_s(\mathbf{r}_1, \mathbf{r}_2)}{2}, \quad (10)$$

with

$$J_s(\mathbf{r}_1, \mathbf{r}_2) = - \sum_{i,j} \left[f_i^{\sigma_i^*}(\mathbf{r}_1) f_j^{\sigma_j^*}(\mathbf{r}_2) f_j^{\sigma_j}(\mathbf{r}_1) f_i^{\sigma_i}(\mathbf{r}_2) \delta_{\sigma_i, \sigma_j} \right]. \quad (11)$$

The expression for the non-interacting Coulomb energy reads as

$$U_s^{\text{QM}}[n] = \frac{1}{2} \int \int \frac{n(\mathbf{r}_1)n(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 + \frac{1}{2} \int \int \frac{J_s(\mathbf{r}_1, \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2. \quad (12)$$

The non-interacting Coulomb energy within the Kohn-Sham system, by construction self-interaction free, can be obtained by replacing the classical Hartree energy (Eq. (4)) by the quantum mechanical expression (Eq. (12)). The energy functional (Eq.(1)) becomes

$$E[n] = \int v(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} + T_s[n] + U_s^{\text{QM}}[n] + E_c[n]. \quad (13)$$

The exchange-correlation functional is then only the correlation energy, being the difference between the Kohn-Sham and the true system, or can be seen as the difference between using the non-interacting and interacting pair density. In the same way as described above, the equation for the Kohn-Sham potential reads

$$v_{\text{KS}}(\mathbf{r}) = v(\mathbf{r}) + \frac{\delta U_s^{\text{QM}}[n]}{\delta n(\mathbf{r})} + \frac{\delta E_c[n]}{\delta n(\mathbf{r})}. \quad (14)$$

The task now becomes the calculation of the functional derivatives with respect to the density. The form of the correlation functional is generally unknown, so that approximations have to be made. In the following we concentrate on the determination of the functional derivative of the non-interacting Coulomb energy.

For the Hartree term, the derivative represents a trivial task because the expression depends explicitly on the density itself and one obtains the well known Hartree potential,

$$V_H(\mathbf{r}) = \frac{\delta}{\delta n(\mathbf{r})} \frac{1}{2} \int \int \frac{n(\mathbf{r}_1) n(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 = \int \frac{n(\mathbf{r}_1)}{|\mathbf{r} - \mathbf{r}_1|} d\mathbf{r}_1. \quad (15)$$

On the other hand, that functional derivative of the exchange term in Eq. (11) is not obvious because its expression depends only implicitly on the density through the density dependence of the orbitals. The only other method used so far to obtain this derivative is that of the optimized effective potential (OEP) [9, 10].

Recently, we suggested an alternative and simple method to obtain the exchange potential [7, 8]. The basic idea is to expand the occupied Kohn-Sham orbitals, $f_j^\sigma(\mathbf{r})$, forming the density, in a complete and orthonormal basis set [11, 12], also known as the Harriman orbitals or equidensity basis, whose elements are written explicitly in terms of the density allowing the performance of functional derivatives with respect to that quantity. In the suggested procedure, we expand the Kohn-Sham orbitals in that basis,

$$f_j^\sigma(\mathbf{r}) = \sum_{\mathbf{k}} a_{\mathbf{k}}^{j,\sigma} \phi_{\mathbf{k}}^\sigma(\mathbf{r}, [n^\sigma]), \quad (16)$$

where the $a_{\mathbf{k}}^{j,\sigma}$ are expansion coefficients and the elements of the equidensity basis, $\phi_{\mathbf{k}}^\sigma(\mathbf{r}, [n^\sigma])$, are given by the expression

$$\phi_{\mathbf{k}}^\sigma(\mathbf{r}, [n^\sigma]) = \sqrt{\frac{n^\sigma(\mathbf{r})}{N^\sigma}} e^{i\mathbf{k}\cdot\mathbf{R}^\sigma(\mathbf{r};[n^\sigma])}, \quad (17)$$

labeled by a set for three signed integers $\mathbf{k} = \{k_1, k_2, k_3\}$. The \mathbf{R} are defined by normalized integrals over the density, successively integrating over the coordinates. For details in Cartesian coordinates we refer to previous work [8]. The \mathbf{R} for spherical coordinates will be defined and discussed in the next section.

In order to calculate the exchange potential, we obtain the derivative of $J_s(\mathbf{r}_1, \mathbf{r}_2)$ with respect to the density by replacing the orbitals in the exchange term by their expanded forms in (16) and perform the derivatives through the product rule.

We refer in the following the procedure how the functional derivative is obtained as the self-interaction free (SIF) method.

2.3. Formulation in Spherical Coordinates

We define the equidensity basis in spherical coordinates in analogy to the formulation in Cartesian coordinates, discussed in detail in [8]. For practical reasons, we define the vectors \mathbf{R} occurring in the definition of the equidensity basis, Eq. (17), by integrating first over r , then over θ , and finally over ϕ , as follows,

$$\begin{aligned} R_1^\sigma(r, \theta, \phi; [n^\sigma]) &= \frac{2\pi}{N^\sigma(\theta, \phi; [n^\sigma])} \int_0^r n^\sigma(r', \theta, \phi; [n^\sigma]) r'^2 dr' \\ R_2^\sigma(\theta, \phi; [n^\sigma]) &= \frac{2\pi}{N^\sigma(\phi; [n^\sigma])} \int_0^\theta N^\sigma(\theta', \phi; [n^\sigma]) \sin(\theta') d\theta' \\ R_3^\sigma(\phi; [n^\sigma]) &= \frac{2\pi}{N^\sigma[n^\sigma]} \int_0^\phi N^\sigma(\phi'; [n^\sigma]) d\phi', \end{aligned} \quad (18)$$

with

$$\begin{aligned}
N^\sigma(\theta, \phi; [n^\sigma]) &= \int_0^\infty n^\sigma(r', \theta, \phi; [n^\sigma]) r'^2 dr' \\
N^\sigma(\phi; [n^\sigma]) &= \int_0^\pi N^\sigma(\theta', \phi; [n^\sigma]) \sin(\theta') d\theta' \\
N^\sigma[n^\sigma] &= \int_0^{2\pi} N^\sigma(\phi'; [n^\sigma]) d\phi'.
\end{aligned} \tag{19}$$

The two basis sets, in Cartesian and spherical coordinates, are not the same, but both of them are complete such that one can find a transformation to express one basis in terms of the other. Nevertheless, in this paper we do not attempt to express the basis in Cartesian coordinates in spherical coordinates. We have defined a new basis for spherical coordinates which is built in a similar way as the Cartesian one, by successively integrating over the coordinates. We also point out, many choices to build an equidensity basis are possible.

In [8] we derived an expression for the exchange potential corresponding to the non-interacting Coulomb energy of the Kohn-Sham system,

$$v_x^\sigma(\mathbf{r}') = -2\mathfrak{K} \sum_{ij}^N \delta_{\sigma_i, \sigma_j, \sigma} \int I^{ij}(\mathbf{r}) f_j^*(\mathbf{r}) \frac{\delta f_i(\mathbf{r})}{\delta n^\sigma(\mathbf{r}')} d\mathbf{r}, \tag{20}$$

where the functional derivative of an orbital is given by the expression [8],

$$\frac{\delta f_i^\sigma(\mathbf{r})}{\delta n^\sigma(\mathbf{r}')} = \frac{\delta(\mathbf{r} - \mathbf{r}')}{2n^\sigma(\mathbf{r})} f_i^\sigma(\mathbf{r}) - \frac{f_i^\sigma(\mathbf{r})}{2N^\sigma} + \frac{\delta \mathbf{R}(\mathbf{r}, [n^\sigma])}{\delta n^\sigma(\mathbf{r}')} \cdot \mathbf{Q}^{i, \sigma}. \tag{21}$$

The second term (from the derivative of the normalization) leads to a constant shift in the potential and can be neglected. Furthermore, the quantities I^{ij} and \mathbf{Q} are defined in the same way as in [8] as

$$I^{ij}(\mathbf{r}_1) : = \int \frac{f_i^*(\mathbf{r}_2) f_j(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_2, \tag{22}$$

$$\mathbf{Q}^{i, \sigma} = \sum_{\mathbf{k}} i \mathbf{k} a_{\mathbf{k}}^{i, \sigma} \phi_{\mathbf{k}}(\mathbf{r}, [n^\sigma]). \tag{23}$$

In Appendix A and Appendix B we derive the expressions in spherical coordinates for the products $\frac{\delta \mathbf{R}(\mathbf{r}, [n^\sigma])}{\delta n^\sigma(\mathbf{r}')} \cdot \mathbf{Q}^{i, \sigma}$. As shown in [8], the infinite sum within \mathbf{Q} can be replaced by an analytic expression containing only the density, the orbitals and the spatial derivatives of these quantities. The exchange potential can then be obtained using Eq. (20) by simple integration. In this formulation, neither the basis functions $\phi_{\mathbf{k}}$ nor the expansion coefficients $a_{\mathbf{k}}$ have to be evaluated to obtain the exchange potential. The basis was used in the derivation but dropped out in final expressions.

2.3.1. Special Case: Spherical Densities

If the density is spherically symmetric, $n^\sigma(r, \theta, \phi) = n^\sigma(r)$, the N^σ (Eqs. (19)) reduce to:

$$\begin{aligned}
N^\sigma(\theta, \phi; [n^\sigma]) &= \frac{N^\sigma}{4\pi} \\
N^\sigma(\phi; [n^\sigma]) &= \frac{N^\sigma}{2\pi} \\
N^\sigma[n^\sigma] &= N^\sigma.
\end{aligned} \tag{24}$$

Then the \mathbf{R} (Eqn. (18)) become

$$\begin{aligned}
R_1^\sigma(r, \theta, \phi; [n^\sigma]) &= \frac{8\pi^2}{N^\sigma} \int_0^r n^\sigma(r'; [n^\sigma]) r'^2 dr' \\
R_2^\sigma(\theta, \phi; [n^\sigma]) &= \pi(1 - \cos(\theta)) \\
R_3^\sigma(\phi; [n^\sigma]) &= \phi.
\end{aligned} \tag{25}$$

Some of their spatial derivatives (see Appendix A.1) vanish,

$$0 = \beta_{12} = \beta_{13} = \beta_{23}, \quad (26)$$

and the functions g defined in Eqs. (B.7) reduce to

$$\begin{aligned} g_r^i &= \frac{\partial f^i}{\partial r} - \frac{f_i(\mathbf{r})}{2n(\mathbf{r})} \frac{\partial n(\mathbf{r})}{\partial r} \\ g_\theta^i &= \frac{\partial f^i}{\partial \theta} \\ g_\phi^i &= \frac{\partial f^i}{\partial \phi} \end{aligned}$$

Then the \mathbf{Q} become

$$\mathbf{Q}_r^\sigma = \frac{1}{r^2} \frac{N^\sigma}{8\pi^2 n^\sigma(r)} g_r \hat{e}_r \quad (27)$$

$$\mathbf{Q}_\theta^\sigma = \frac{1}{\sin(\theta)} \frac{1}{\pi} \frac{\partial f}{\partial \theta} \hat{e}_\theta \quad (28)$$

$$\mathbf{Q}_\phi^\sigma = \frac{\partial f}{\partial \phi} \hat{e}_\phi, \quad (29)$$

where \hat{e}_r , \hat{e}_θ and \hat{e}_ϕ are unit vectors in the direction of r , θ , and ϕ . The components of the product $\frac{\delta \mathbf{R}}{\delta n} \cdot \mathbf{Q}$ simplify to

$$\begin{aligned} \frac{\delta R_1(\mathbf{r})}{\delta n(\mathbf{r}'')} \cdot \mathbf{Q}_r(\mathbf{r}) &= \frac{1}{r^2 \sin(\theta)} \delta(\theta - \theta'') \delta_{2\pi}(\phi - \phi'') \left\{ \frac{1}{n(r)} \left[\frac{\partial f}{\partial r} - \frac{f(\mathbf{r})}{2n^\sigma(\mathbf{r})} \frac{\partial n^\sigma(\mathbf{r})}{\partial r} \right] \left[\Theta(r - r'') - \frac{R_1(r, \theta, \phi)}{2\pi} \right] \right\} \\ \frac{\delta R_2(\mathbf{r})}{\delta n(\mathbf{r}'')} \cdot \mathbf{Q}_\theta(\mathbf{r}) &= \frac{1}{r^2 \sin(\theta)} \delta_{2\pi}(\phi - \phi'') \left[4\pi r^2 \frac{1}{N} \frac{\partial f}{\partial \theta} \right] \left[\Theta(\theta - \theta'') - \frac{(1 - \cos(\theta))}{2} \right] \\ \frac{\delta R_3(\mathbf{r})}{\delta n(\mathbf{r}'')} \cdot \mathbf{Q}_\phi(\mathbf{r}) &= \frac{2\pi}{N} \left[\Theta(\phi - \phi'') - \frac{\phi}{2\pi} \right] \frac{\partial f}{\partial \phi}. \end{aligned} \quad (30)$$

The notation $\delta_{2\pi}(\cdot)$ is used to denote the finite support of the argument between 0 and 2π .

2.3.2. Special Case: Spherical Orbitals

If the orbitals are assumed to be spherically symmetric, $f_i(\mathbf{r}) = f_i(r)$, or simply s-orbitals, then it follows immediately that several terms vanish:

$$0 = \mathbf{Q}_\theta = \mathbf{Q}_\phi = \frac{\delta R_2(\mathbf{r})}{\delta n(\mathbf{r}'')} \cdot \mathbf{Q}_\theta(\mathbf{r}) = \frac{\delta R_3(\mathbf{r})}{\delta n(\mathbf{r}'')} \cdot \mathbf{Q}_\phi(\mathbf{r}). \quad (31)$$

The expression for the exchange potential (Eq. (20)) then reads

$$\begin{aligned} x_x^\sigma(\mathbf{r}'') &= -2\mathfrak{K} \sum_{i,j} \delta_{\sigma_i, \sigma_j, \sigma} \int \int \int I^{ij}(\mathbf{r}) f_j^*(\mathbf{r}) \frac{f_i(\mathbf{r})}{\delta n(\mathbf{r}'')} r^2 \sin(\theta) dr d\theta d\phi \\ &= -2\mathfrak{K} \sum_{i,j} \delta_{\sigma_i, \sigma_j, \sigma} \int \int \int I^{ij}(\mathbf{r}) f_j^*(\mathbf{r}) \left[\frac{\delta(\mathbf{r} - \mathbf{r}'')}{r^2 \sin \theta} \frac{f_i(\mathbf{r})}{2n(\mathbf{r})} \right. \\ &\quad \left. + \frac{1}{r^2 \sin(\theta)} \delta(\theta - \theta'') \delta_{2\pi}(\phi - \phi'') \times \left\{ \right. \right. \\ &\quad \left. \left. \frac{1}{n(r)} \left[\frac{\partial f}{\partial r} - \frac{f(\mathbf{r})}{2n^\sigma(\mathbf{r})} \frac{\partial n^\sigma(\mathbf{r})}{\partial r} \right] \left[\Theta(r - r'') - \frac{R_1(r)}{2\pi} \right] \right\} \right] r^2 \sin(\theta) dr d\theta d\phi. \end{aligned} \quad (32)$$

All quantities depend only on r (but not on θ and ϕ), and performing the integration over θ and ϕ we obtain the expression,

$$v_x^\sigma(r'') = -2\mathfrak{K} \sum_{i,j} \delta_{\sigma_i, \sigma_j, \sigma} \int I^{ij}(r) f_j^*(r) \left[\delta(r-r'') \frac{f_i(r)}{2n(r)} + \left\{ \frac{1}{n(r)} \left[\frac{\partial f_i}{\partial r} - \frac{f_i(r)}{2n^\sigma(r)} \frac{\partial n^\sigma(r)}{\partial r} \right] \left[\Theta(r-r'') - \frac{R_1(r)}{2\pi} \right] \right\} \right] dr. \quad (33)$$

The term containing R_1 contributes only a constant to the potential and can be neglected. Finally, for the case of spherical orbitals, the exchange potential takes the form,

$$v_x^\sigma(r'') = -2\mathfrak{K} \sum_{i,j} \delta_{\sigma_i, \sigma_j, \sigma} \int I^{ij}(r) f_j^*(r) \left[\delta(r-r'') \frac{f_i(r)}{2n(r)} + \frac{\Theta(r-r'')}{n(r)} \left\{ \frac{\partial f_i}{\partial r} - \frac{f_i(r)}{2n^\sigma(r)} \frac{\partial n^\sigma(r)}{\partial r} \right\} \right] dr. \quad (34)$$

This result is formally identical to the one we obtained for the one-dimensional case where Cartesian coordinates were used, as discussed in reference [8].

2.4. Virial Theorem

The Virial theorem for the exchange contribution is a relationship between the exchange energy and the corresponding exchange potential, and provides a necessary although not sufficient condition between the two quantities. The exchange energy is given by the expression,

$$E_x = -\frac{1}{2} \sum_{ij} \int I^{ij}(\mathbf{r}) f_j^*(\mathbf{r}) f_i(\mathbf{r}) \delta_{\sigma_i, \sigma_j} r^2 \sin(\theta) dr d\theta d\phi, \quad (35)$$

where the energy from the Virial theorem, E_V , using the exchange potential reads as

$$E_V = - \int n(\mathbf{r}) \mathbf{r} \cdot \nabla_{v_x}(\mathbf{r}) r^2 \sin(\theta) dr d\theta d\phi. \quad (36)$$

The necessary condition, that the exchange potential is the functional derivative of the exchange energy with respect to the density demands the Virial energy E_V to be equal to the exchange energy E_x .

We show in detail in Appendix C, for spherical orbitals, that indeed the derived form for the exchange potential satisfies the equality, $E_V = E_x$.

3. Application to Atoms

The formulation in spherical coordinates to obtain the exchange potential allows an efficient calculation of the ground state energies of the atoms throughout the periodic table within the exchange only (correlation energy set to zero) mode of the Kohn-Sham equations. In this case, the results are independent of a particular choice of the approximation of the correlation energy and can be used as a benchmark for other formulations that take account of correlation. Atomic configurations as shown in Table C.1 are used, where the atomic configurations for some of the higher elements ($Z > 100$) are assumed.

We solve the Kohn-Sham equations (3) self-consistently using the potential corresponding to the quantum mechanical expression for the Coulomb energy (Eq. (7)), as shown in detail in Section 2. Orbitals entering Eq. (20) to obtain the exchange potential are treated generally as non-spherical, resulting in a non-spherical exchange potential for open-shell atoms, while to iterate the Kohn-Sham equations only the spherical part of the potential is used.

The spherical part of the exchange potential for Xenon, Gold, Radon, Californium, Livermorium and Ununoctium is shown in Fig. C.2. The first column shows the exchange potential as a function of the radial distance from the nucleus, r , measured on a logarithmic scale. This demonstrates the correct and expected behavior at the origin: The spatial derivative has to vanish. Pictures in the middle column show the same potential multiplied by the distance, r . We see that in the asymptotic region, all potentials decay as $1/r$, as expected. In the third column on the right, the spin-resolved densities are plotted as appropriate, multiplied by $4\pi r^2$.

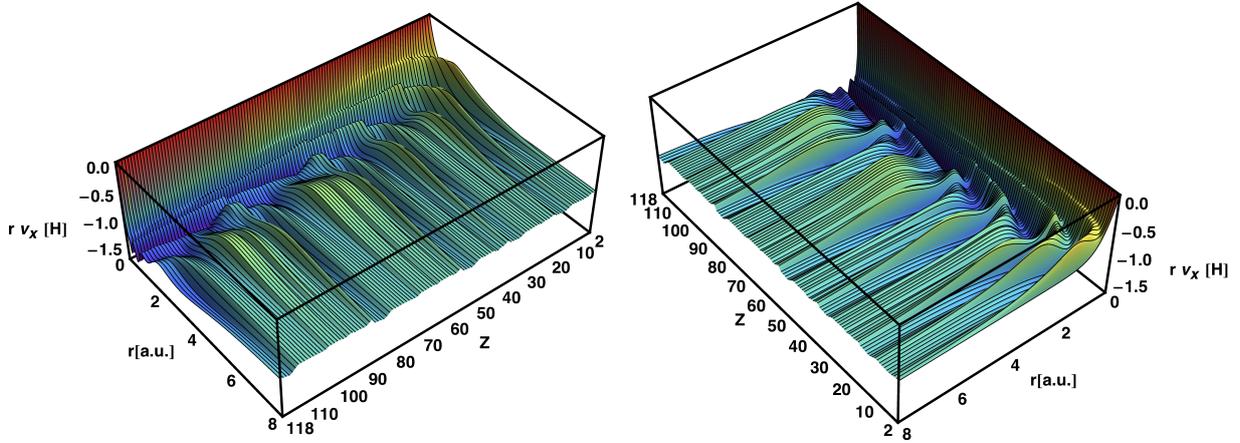


Figure 1: SIF exchange potentials multiplied by r , the distance from the nucleus, for the atomic series Helium ($Z = 2$) to Ununoctium ($Z = 118$). The figures show the same data, at a different angle. The colored surface is for illustration, and exchange potentials are only meaningful for integer Z values, marked by the black lines.

For illustration, in Fig. 1, we show in a three-dimensional schematic diagram all exchange potentials multiplied by r from Helium to Ununoctium. Total energies for all atoms calculated within the exchange-only mode using the SIF formalism are given in Table C.1. Because of the neglect of the correlation energy, all energies lie above the true ground state energy. Generally, energies obtained by the SIF method are slightly higher than those obtained by a Hartree-Fock calculation due to their different constraints.

We mention that the exchange potentials and energies for atoms obtained using the equidensity in spherical coordinates are identical to those previously obtained [8], where a formulation in Cartesian coordinates was used. From a physical standpoint, this is quite obvious: Results must be independent of the chosen coordinate system, although the expressions for the equidensity basis and the resulting equations for the potential are different in two different coordinate systems.

Finally, we point out that the SIF energies and potentials coincide with those obtained by Sahni, Li and Harbola [13] for spherical systems where their method can be applied.

4. Conclusions

In this paper, we report algebraic details of a method that allows the self-interaction free implementation of DFT, and shown the results of calculations of the ground-state energies across the atoms in the periodic table, from He to Uuo. This procedure opens the path to methodology that may overcome long-existing difficulties in the study of electronic structure of condensed matter. Furthermore, we provided proof that the SIF method satisfies the Virial theorem for systems with spherical orbitals.

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Appendix A. Derivatives of the R

Appendix A.1. Spatial Derivatives

For completeness, we provide all spatial derivatives of the functions \mathbf{R} (Eqs.(18)) in spherical coordinates.

$$\beta_{i\alpha} := \nabla_\alpha R_i \quad (\text{A.1})$$

$$\beta_{11} := \nabla_r R_1 = 2\pi r^2 \frac{n(r, \theta, \phi)}{N(\theta, \phi)} \hat{e}_r \quad (\text{A.2})$$

$$\beta_{12} := \nabla_\theta R_1 = \frac{1}{N(\theta, \phi)} \left[2\pi \int_0^r dr' r'^2 \nabla_\theta n(r', \theta, \phi) - R_1 \int_0^\infty dr' r'^2 \nabla_\theta n(r', \theta, \phi) \right] \quad (\text{A.3})$$

$$= \frac{1}{N(\theta, \phi)} \frac{1}{r} \left[2\pi \int_0^r dr' r'^2 \frac{\partial n(r', \theta, \phi)}{\partial \theta} - R_1 \int_0^\infty dr' r'^2 \frac{\partial n(r', \theta, \phi)}{\partial \theta} \right] \hat{e}_\theta \quad (\text{A.4})$$

$$\beta_{13} := \nabla_\phi R_1 = \frac{1}{N(\theta, \phi)} \left[2\pi \int_0^r dr' r'^2 \nabla_\phi n(r', \theta, \phi) - R_1 \int_0^\infty dr' r'^2 \nabla_\phi n(r', \theta, \phi) \right]$$

$$= \frac{1}{N(\theta, \phi)} \frac{1}{r \sin(\theta)} \left[2\pi \int_0^r dr' r'^2 \frac{\partial n(r', \theta, \phi)}{\partial \phi} - R_1 \int_0^\infty dr' r'^2 \frac{\partial n(r', \theta, \phi)}{\partial \phi} \right] \hat{e}_\phi$$

$$\beta_{21} := \nabla_r R_2 = 0 \hat{e}_r \quad (\text{A.5})$$

$$\beta_{22} := \nabla_\theta R_2 = 2\pi \sin(\theta) \frac{1}{r} \frac{N(\theta, \phi)}{N(\phi)} \hat{e}_\theta \quad (\text{A.6})$$

$$\beta_{23} := \nabla_\phi R_2 = \frac{1}{N(\phi)} \left[2\pi \int_0^\theta d\theta' \sin(\theta') \int_0^\infty dr' r'^2 \nabla_\phi n(r', \theta', \phi) \right. \\ \left. - R_2 \int_0^\pi d\theta' \sin(\theta') \int_0^\infty dr' r'^2 \nabla_\phi n(r', \theta', \phi) \right] \quad (\text{A.7})$$

$$= \frac{1}{N(\phi)} \frac{1}{r \sin(\theta)} \left[2\pi \int_0^\theta d\theta' \sin(\theta') \int_0^\infty dr' r'^2 \frac{\partial n(r', \theta', \phi)}{\partial \phi} \right. \\ \left. - R_2 \int_0^\pi d\theta' \sin(\theta') \int_0^\infty dr' r'^2 \frac{\partial n(r', \theta', \phi)}{\partial \phi} \right] \hat{e}_\phi \quad (\text{A.8})$$

$$\beta_{31} := \nabla_r R_3 = 0 \hat{e}_r \quad (\text{A.9})$$

$$\beta_{32} := \nabla_\theta R_3 = 0 \hat{e}_\theta \quad (\text{A.10})$$

$$\beta_{33} := \nabla_\phi R_3 = 2\pi \frac{1}{r \sin(\theta)} \frac{N(\phi)}{N} \hat{e}_\phi \quad (\text{A.11})$$

The Jacobian then is given by

$$\det \beta = \det \begin{vmatrix} \nabla_r R_1 & \nabla_\theta R_1 & \nabla_\phi R_1 \\ 0 & \nabla_\theta R_2 & \nabla_\phi R_2 \\ 0 & 0 & \nabla_\phi R_3 \end{vmatrix} = \frac{(2\pi)^3}{N} n(r, \theta, \phi). \quad (\text{A.12})$$

Appendix A.2. Functional Derivatives of the \mathbf{R}

The delta function in spherical coordinates reads as

$$\delta(\mathbf{r} - \mathbf{r}') = \frac{1}{r^2 \sin(\theta)} \delta(r - r') \delta(\theta - \theta') \delta_{2\pi}(\phi - \phi'), \quad (\text{A.13})$$

where $\delta_{2\pi}$ is defined in $[0, 2\pi)$, in order to take the periodicity of the function into account.

Straightforward functional differentiations lead to the expressions:

$$\begin{aligned}
\frac{\delta R_1(r, \theta, \phi; [n^\sigma])}{\delta n(\mathbf{r}'')} &= 2\pi \frac{\delta}{\delta n(\mathbf{r}'')} \frac{\int_0^r dr' r'^2 n(r', \theta, \phi, [n^\sigma])}{\int_0^\infty dr' r'^2 n(r', \theta, \phi, [n^\sigma])} \\
&= 2\pi \frac{\int_0^r dr' \frac{r'^2}{r'^2 \sin(\theta)} \delta(r' - r'') \delta(\theta - \theta'') \delta_{2\pi}(\phi - \phi'')}{\int_0^\infty dr' r'^2 n(r', \theta, \phi; [n^\sigma])} \\
&\quad - 2\pi \int_0^\infty dr' \frac{r'^2}{r'^2 \sin(\theta)} \delta(r' - r'') \delta(\theta - \theta'') \delta_{2\pi}(\phi - \phi'') \\
&\quad \times \frac{\int_0^r dr' r'^2 n(r', \theta, \phi; [n^\sigma])}{\left[\int_0^\infty dr' r'^2 n(r', \theta, \phi; [n^\sigma]) \right]^2} \\
&= \frac{\delta(\theta - \theta'') \delta_{2\pi}(\phi - \phi'')}{\sin(\theta) N(\theta, \phi; [n^\sigma])} \left[2\pi \Theta(r - r'') - R_1(r, \theta, \phi; [n^\sigma]) \right],
\end{aligned}$$

$$\begin{aligned}
\frac{\delta R_2(\theta, \phi; [n^\sigma])}{\delta n(\mathbf{r}'')} &= 2\pi \frac{\delta}{\delta n(\mathbf{r}'')} \frac{\int_0^\theta d\theta' \sin(\theta') \int_0^\infty dr' r'^2 n(r', \theta', \phi, [n^\sigma])}{\int_0^\pi d\theta' \sin(\theta') \int_0^\infty dr' r'^2 n(r', \theta', \phi, [n^\sigma])} \\
&= 2\pi \frac{\int_0^\theta d\theta' \sin(\theta') \int_0^\infty dr' \frac{r'^2}{r'^2 \sin(\theta')} \delta(r' - r'') \delta(\theta' - \theta'') \delta_{2\pi}(\phi - \phi'')}{\int_0^\pi d\theta' \sin(\theta') \int_0^\infty dr' r'^2 n(r', \theta', \phi, [n^\sigma])} \\
&\quad - 2\pi \int_0^\pi d\theta' \sin(\theta') \int_0^\infty dr' \frac{r'^2}{r'^2 \sin(\theta')} \delta(r' - r'') \delta(\theta' - \theta'') \delta_{2\pi}(\phi - \phi'') \\
&\quad \times \frac{\int_0^\theta d\theta' \sin(\theta') \int_0^\infty dr' r'^2 n(r', \theta', \phi, [n^\sigma])}{\left[\int_0^\pi d\theta' \sin(\theta') \int_0^\infty dr' r'^2 n(r', \theta', \phi, [n^\sigma]) \right]^2} \\
&= \frac{\delta_{2\pi}(\phi - \phi'')}{N(\phi, [n^\sigma])} \left[2\pi \Theta(\theta - \theta'') - R_2(\theta, \phi; [n^\sigma]) \right],
\end{aligned}$$

and

$$\begin{aligned}
\frac{\delta R_3(\phi; [n^\sigma])}{\delta n(\mathbf{r}'')} &= 2\pi \frac{\delta}{\delta n(\mathbf{r}'')} \frac{\int_0^\phi d\phi' \int_0^\pi d\theta' \sin(\theta') \int_0^\infty dr' r'^2 n(r', \theta', \phi', [n^\sigma])}{\int_0^{2\pi} d\phi' \int_0^\pi d\theta' \sin(\theta') \int_0^\infty dr' r'^2 n(r', \theta', \phi', [n^\sigma])} \\
&= 2\pi \frac{\int_0^\phi d\phi' \int_0^\pi d\theta' \sin(\theta') \int_0^\infty dr' \frac{r'^2}{r'^2 \sin(\theta')} \delta(r' - r'') \delta(\theta' - \theta'') \delta_{2\pi}(\phi' - \phi'')}{\int_0^{2\pi} d\phi' \int_0^\pi d\theta' \sin(\theta') \int_0^\infty dr' r'^2 n(r', \theta', \phi', [n^\sigma])} \\
&\quad - 2\pi \int_0^{2\pi} d\phi' \int_0^\pi d\theta' \sin(\theta') \int_0^\infty dr' \frac{r'^2}{r'^2 \sin(\theta')} \delta(r' - r'') \delta(\theta' - \theta'') \delta_{2\pi}(\phi' - \phi'') \\
&\quad \times \frac{\int_0^\phi d\phi' \int_0^\pi d\theta' \sin(\theta') \int_0^\infty dr' r'^2 n(r', \theta', \phi', [n^\sigma])}{\left[\int_0^{2\pi} d\phi' \int_0^\pi d\theta' \sin(\theta') \int_0^\infty dr' r'^2 n(r', \theta', \phi', [n^\sigma]) \right]^2} \\
&= \frac{1}{N^\sigma} \left[2\pi \Theta(\phi - \phi'') - R_3(\phi; [n^\sigma]) \right].
\end{aligned}$$

Appendix B. On the Calculation of the Infinite Sums

In spherical coordinates, the gradient is given by the expression

$$\nabla = \frac{\partial}{\partial r} \hat{e}_r + \frac{1}{r} \frac{\partial}{\partial \theta} \hat{e}_\theta + \frac{1}{r \sin(\theta)} \frac{\partial}{\partial \phi} \hat{e}_\phi. \tag{B.1}$$

We use the notation

$$\nabla_r f(r, \theta, \phi) = \frac{\partial f(r, \theta, \phi)}{\partial r} \hat{e}_r \quad (\text{B.2})$$

$$\nabla_\theta f(r, \theta, \phi) = \frac{1}{r} \frac{\partial f(r, \theta, \phi)}{\partial \theta} \hat{e}_\theta \quad (\text{B.3})$$

$$\nabla_\phi f(r, \theta, \phi) = \frac{1}{r \sin(\theta)} \frac{\partial f(r, \theta, \phi)}{\partial \phi} \hat{e}_\phi. \quad (\text{B.4})$$

The gradient of an orbital, f , decomposed into the equidensity basis (16) is given by

$$\nabla_\alpha f(\mathbf{r}) = \sum_{\mathbf{k}} a_{\mathbf{k}}^\sigma \nabla_\alpha \left[\sqrt{\frac{n^\sigma(\mathbf{r})}{N^\sigma}} e^{i\mathbf{k} \cdot \mathbf{R}(\mathbf{r}, [n^\sigma])} \right] \quad (\text{B.5})$$

$$\begin{aligned} &= \frac{f(\mathbf{r})}{2n^\sigma(\mathbf{r})} \nabla_\alpha n^\sigma(\mathbf{r}) \\ &+ i \sum_{\mathbf{k}} \phi_{\mathbf{k}}^\sigma(\mathbf{r}, [n^\sigma]) [\mathbf{k} \cdot \nabla_\alpha \mathbf{R}(\mathbf{r}, [n^\sigma])], \end{aligned} \quad (\text{B.6})$$

with $\alpha \in \{r, \theta, \phi\}$. For each orbital we define the quantity g as follows, containing spatial derivatives of the orbitals and the density:

$$\begin{aligned} g_r^{\sigma,i}(\mathbf{r}) &:= \frac{\partial f_i}{\partial r} - \frac{f_i(\mathbf{r})}{2n^\sigma(\mathbf{r})} \frac{\partial n^\sigma(\mathbf{r})}{\partial r} \\ g_\theta^{\sigma,i}(\mathbf{r}) &:= \frac{\partial f_i}{\partial \theta} - \frac{f_i(\mathbf{r})}{2n^\sigma(\mathbf{r})} \frac{\partial n^\sigma(\mathbf{r})}{\partial \theta} \\ g_\phi^{\sigma,i}(\mathbf{r}) &:= \frac{\partial f_i}{\partial \phi} - \frac{f_i(\mathbf{r})}{2n^\sigma(\mathbf{r})} \frac{\partial n^\sigma(\mathbf{r})}{\partial \phi}. \end{aligned} \quad (\text{B.7})$$

Appendix B.1. Derivation of the Q

We calculate the spatial derivative of an orbital with respect to r (Eq. (B.6)), where $\beta_{21} = \beta_{31} = 0$ (see Appendix A.1):

$$\nabla_r f = \frac{f(\mathbf{r})}{2n^\sigma(\mathbf{r})} \nabla_r n^\sigma(\mathbf{r}) + \underbrace{\sum_{\mathbf{k}} a_{\mathbf{k}}^\sigma \phi_{\mathbf{k}}^\sigma(\mathbf{r})(ik_1)}_{Q_r} \underbrace{\left(2\pi r^2 \frac{n^\sigma(\mathbf{r})}{N^\sigma(\theta, \phi)} \right)}_{\beta_{11}} \hat{e}_r. \quad (\text{B.8})$$

This allows us to calculate the quantity Q_r which is equivalent to the first part of the infinite sum:

$$\begin{aligned} Q_r^\sigma &= \sum_{\mathbf{k}} a_{\mathbf{k}}^\sigma \phi_{\mathbf{k}}^\sigma(\mathbf{r})(ik_1) \hat{e}_r = \frac{1}{r^2} \frac{N^\sigma(\theta, \phi)}{2\pi n^\sigma(\mathbf{r})} \left[\nabla_r f - \frac{f(\mathbf{r})}{2n^\sigma(\mathbf{r})} \nabla_r n^\sigma(\mathbf{r}) \right] = \frac{1}{r^2} \frac{N^\sigma(\theta, \phi)}{2\pi n^\sigma(\mathbf{r})} \left[\frac{\partial f}{\partial r} - \frac{f(\mathbf{r})}{2n^\sigma(\mathbf{r})} \frac{\partial n^\sigma(\mathbf{r})}{\partial r} \right] \hat{e}_r \\ &= \frac{1}{r^2} \frac{N^\sigma(\theta, \phi)}{2\pi n^\sigma(\mathbf{r})} [g_r] \hat{e}_r. \end{aligned} \quad (\text{B.9})$$

In the same way we calculate Q_θ using the gradient with respect to θ :

$$\nabla_\theta f = \frac{f(\mathbf{r})}{2n^\sigma(\mathbf{r})} \nabla_\theta n^\sigma(\mathbf{r}) + \underbrace{\sum_{\mathbf{k}} a_{\mathbf{k}}^\sigma \phi_{\mathbf{k}}^\sigma(\mathbf{r})(ik_1)}_{Q_r} \underbrace{\beta_{12}^\sigma}_{Q_\theta} + \underbrace{\sum_{\mathbf{k}} a_{\mathbf{k}}^\sigma \phi_{\mathbf{k}}^\sigma(\mathbf{r})(ik_2)}_{Q_\theta} \underbrace{2\pi \sin(\theta) \frac{1}{r} \frac{N^\sigma(\theta, \phi)}{N^\sigma(\phi)}}_{\beta_{22}} \hat{e}_\theta, \quad (\text{B.10})$$

$$\begin{aligned}
Q_\theta^\sigma &= \sum_{\mathbf{k}} a_{\mathbf{k}}^\sigma \phi_{\mathbf{k}}^\sigma(\mathbf{r})(ik_2) \hat{e}_\theta = \frac{r}{\sin(\theta)} \frac{N^\sigma(\phi)}{2\pi N^\sigma(\theta, \phi)} \left[\nabla_\theta f - \frac{f(\mathbf{r})}{2n^\sigma(\mathbf{r})} \nabla_\theta n^\sigma(\mathbf{r}) - \frac{Q_r^\sigma}{\hat{e}_r} \beta_{12}^\sigma \right] \\
&= \frac{r}{\sin(\theta)} \frac{N^\sigma(\phi)}{2\pi N^\sigma(\theta, \phi)} \left[\frac{1}{r} \frac{\partial f}{\partial \theta} \hat{e}_\theta - \frac{f(\mathbf{r})}{2n^\sigma(\mathbf{r})} \frac{1}{r} \frac{\partial n^\sigma(\mathbf{r})}{\partial \theta} \hat{e}_\theta - \frac{Q_r^\sigma}{\hat{e}_r} \beta_{12}^\sigma \right] \\
&= \frac{1}{\sin(\theta)} \frac{N^\sigma(\phi)}{2\pi N^\sigma(\theta, \phi)} \left[\frac{\partial f}{\partial \theta} \hat{e}_\theta - \frac{f(\mathbf{r})}{2n^\sigma(\mathbf{r})} \frac{\partial n^\sigma(\mathbf{r})}{\partial \theta} \hat{e}_\theta - \frac{Q_r^\sigma}{\hat{e}_r} (r \beta_{12}^\sigma) \right] \tag{B.11} \\
&= \frac{1}{\sin(\theta)} \frac{N^\sigma(\phi)}{2\pi N^\sigma(\theta, \phi)} \left[g_\theta \hat{e}_\theta - \frac{Q_r^\sigma}{\hat{e}_r} (r \beta_{12}^\sigma) \right] \tag{B.12}
\end{aligned}$$

Finally, we calculate Q_ϕ using the gradient with respect to ϕ :

$$\begin{aligned}
\nabla_\phi f &= \frac{f(\mathbf{r})}{2n^\sigma(\mathbf{r})} \nabla_\phi n^\sigma(\mathbf{r}) + \underbrace{\sum_{\mathbf{k}} a_{\mathbf{k}}^\sigma \phi_{\mathbf{k}}^\sigma(\mathbf{r})(ik_1) \beta_{13}^\sigma}_{Q_r} \\
&\quad + \underbrace{\sum_{\mathbf{k}} a_{\mathbf{k}}^\sigma \phi_{\mathbf{k}}^\sigma(\mathbf{r})(ik_2) \beta_{23}^\sigma}_{Q_\theta} + \underbrace{\sum_{\mathbf{k}} a_{\mathbf{k}}^\sigma \phi_{\mathbf{k}}^\sigma(\mathbf{r})(ik_3) 2\pi \frac{1}{r \sin(\theta)} \frac{N^\sigma(\phi)}{N^\sigma}}_{\beta_{33}} \hat{e}_\phi, \tag{B.13}
\end{aligned}$$

$$\begin{aligned}
Q_\phi^\sigma &= \sum_{\mathbf{k}} a_{\mathbf{k}}^\sigma \phi_{\mathbf{k}}^\sigma(\mathbf{r})(ik_3) \hat{e}_\phi = \frac{N^\sigma}{2\pi N^\sigma(\phi)} r \sin(\theta) \left[\nabla_\phi f - \frac{f(\mathbf{r})}{2n^\sigma(\mathbf{r})} \nabla_\phi n^\sigma(\mathbf{r}) - \frac{Q_r^\sigma}{\hat{e}_r} \beta_{13}^\sigma - \frac{Q_\theta^\sigma}{\hat{e}_\theta} \beta_{23}^\sigma \right] \\
&= \frac{N^\sigma}{2\pi N^\sigma(\phi)} r \sin(\theta) \left[\frac{1}{r \sin(\theta)} \frac{\partial f}{\partial \phi} - \frac{f(\mathbf{r})}{2n^\sigma(\mathbf{r})} \frac{1}{r \sin(\theta)} \frac{\partial n^\sigma(\mathbf{r})}{\partial \phi} - \frac{Q_r^\sigma}{\hat{e}_r} \beta_{13}^\sigma - \frac{Q_\theta^\sigma}{\hat{e}_\theta} \beta_{23}^\sigma \right] \\
&= \frac{N^\sigma}{2\pi N^\sigma(\phi)} \left[\frac{\partial f}{\partial \phi} \hat{e}_\phi - \frac{f(\mathbf{r})}{2n^\sigma(\mathbf{r})} \frac{\partial n^\sigma(\mathbf{r})}{\partial \phi} \hat{e}_\phi - \frac{Q_r^\sigma}{\hat{e}_r} (r \sin(\theta) \beta_{13}^\sigma) - \frac{Q_\theta^\sigma}{\hat{e}_\theta} (r \sin(\theta) \beta_{23}^\sigma) \right] \\
&= \frac{N^\sigma}{2\pi N^\sigma(\phi)} \left[g_\phi \hat{e}_\phi - \frac{Q_r^\sigma}{N^\sigma(\theta, \phi) \hat{e}_r} N^\sigma(\theta, \phi) (r \sin(\theta) \beta_{13}^\sigma) - \frac{Q_\theta^\sigma}{\hat{e}_\theta} (r \sin(\theta) \beta_{23}^\sigma) \right]
\end{aligned}$$

Appendix B.2. Terms occurring inside the integrals

$$\frac{\delta R_1(\mathbf{r})}{\delta n(\mathbf{r}'')} \cdot Q_r(\mathbf{r}) = \frac{\delta(\theta - \theta'') \delta_{2\pi}(\phi - \phi'')}{\sin(\theta) N(\theta, \phi)} \left[2\pi \Theta(r - r'') - R_1(r, \theta, \phi) \right] \frac{1}{r^2} \frac{N(\theta, \phi)}{2\pi n(\mathbf{r})} [g_r(\mathbf{r})] \tag{B.14}$$

$$= \frac{1}{r^2 \sin(\theta)} \delta(\theta - \theta'') \delta_{2\pi}(\phi - \phi'') \left\{ \underbrace{\frac{g_r(\mathbf{r})}{n(\mathbf{r})}}_{K_1} \left[\Theta(r - r'') - \frac{R_1(r, \theta, \phi)}{2\pi} \right] \right\} \tag{B.15}$$

$$\frac{\delta R_2(\mathbf{r})}{\delta n(\mathbf{r}'')} \cdot Q_\theta(\mathbf{r}) = \frac{\delta_{2\pi}(\phi - \phi'')}{N(\phi)} \left[2\pi \Theta(\theta - \theta'') - R_2(\theta, \phi) \right] \frac{1}{\sin(\theta)} \frac{N(\phi)}{2\pi N(\theta, \phi)} [g_\theta - Q_r(r \beta_{12})] \tag{B.16}$$

$$= \frac{1}{r^2 \sin(\theta)} \delta_{2\pi}(\phi - \phi'') \underbrace{\left[r^2 \frac{g_\theta}{N(\theta, \phi)} - \frac{r^2 Q_r}{N(\theta, \phi)} (r \beta_{12}) \right]}_{K_2} \left[\Theta(\theta - \theta'') - \frac{R_2(\theta, \phi)}{2\pi} \right]$$

$$\frac{r^2 Q_r}{N(\theta, \phi)} = \frac{1}{2\pi} \frac{g_r(\mathbf{r})}{n(\mathbf{r})} = \frac{1}{2\pi} K_1 \tag{B.17}$$

$$\begin{aligned}
\frac{\delta R_3(\mathbf{r})}{\delta n(\mathbf{r}'')} \cdot Q_\phi(\mathbf{r}) &= \frac{1}{N} \left[2\pi \Theta(\phi - \phi'') - R_3(\phi) \right] \frac{N}{2\pi N(\phi)} \left[g_\phi - \frac{Q_r}{N(\theta, \phi)} N(\theta, \phi) \left(r \sin(\theta) \beta_{13} \right) - Q_\theta \left(r \sin(\theta) \beta_{23} \right) \right] \\
&= \frac{1}{r^2 \sin(\theta)} \left[\theta(\phi - \phi'') - \frac{R_3(\phi)}{2\pi} \right] \left[r^2 \sin(\theta) \frac{g_\phi}{N(\phi)} - \frac{\sin(\theta)}{N(\phi)} \underbrace{\frac{r^2 Q_r}{N(\theta, \phi)}}_{\frac{1}{2\pi} K_1} N(\theta, \phi) \left(r \sin(\theta) \beta_{13} \right) \right. \\
&\quad \left. - \frac{r^2 \sin(\theta) Q_\theta}{N(\phi)} \left(r \sin(\theta) \beta_{23} \right) \right] \tag{B.18}
\end{aligned}$$

$$\frac{r^2 \sin(\theta) Q_\theta}{N(\phi)} = \frac{1}{2\pi} \left[r^2 \frac{g_\theta}{N(\theta, \phi)} - \left(\frac{r^2 Q_r}{N(\theta, \phi)} \right) \left(r \beta_{12} \right) \right] = \frac{1}{2\pi} K_2 \tag{B.19}$$

$$\begin{aligned}
\frac{\delta R_3(\mathbf{r})}{\delta n(\mathbf{r}'')} \cdot Q_\phi(\mathbf{r}) &= \frac{1}{r^2 \sin(\theta)} \left[\Theta(\phi - \phi'') - \frac{R_3(\phi)}{2\pi} \right] \left[r^2 \sin(\theta) \frac{g_\phi}{N(\phi)} - \frac{\sin(\theta)}{N(\phi)} \frac{1}{2\pi} K_1 N(\theta, \phi) \left(r \sin(\theta) \beta_{13} \right) \right. \\
&\quad \left. - \frac{1}{2\pi} K_2 \left(r \sin(\theta) \beta_{23} \right) \right] \tag{B.20}
\end{aligned}$$

Appendix C. Virial theorem for spherical orbitals and a spherical density

With A an arbitrary function, we have

$$\nabla f(\mathbf{r}) = \frac{\partial f(r)}{\partial r}; \quad \nabla n(\mathbf{r}) = \frac{\partial n(r)}{\partial r}; \quad \frac{\partial}{\partial r} \int_r^\infty A(r') dr' = -A(r). \tag{C.1}$$

For simplicity, we consider real orbitals and neglect the spin indices, or in other words, the sum over i, j runs only over pairs of equal spin.

$$\begin{aligned}
E_V &= - \int n(\mathbf{r}'') \mathbf{r}'' \cdot \nabla_{(r'')} \left[-2 \sum_{i,j} \int \int \int I^{ij}(\mathbf{r}) f_j(\mathbf{r}) \left[\frac{\delta(\mathbf{r} - \mathbf{r}'')}{r^2 \sin \theta} \frac{f_i(\mathbf{r})}{2n(\mathbf{r})} + \frac{1}{r^2 \sin(\theta)} \delta(\theta - \theta'') \delta_{2\pi}(\phi - \phi'') \right] \right. \\
&\quad \left. \times \left\{ \frac{1}{n(r)} \left[\frac{\partial f}{\partial r} - \frac{f(\mathbf{r})}{2n^\sigma(\mathbf{r})} \frac{\partial n^\sigma(\mathbf{r})}{\partial r} \right] \Theta(r - r'') \right\} \right] r^2 \sin(\theta) dr d\theta d\phi \left] r'^2 \sin(\theta'') dr'' d\theta'' d\phi''. \tag{C.2}
\end{aligned}$$

We use Eq. (C.1), integrate over θ and ϕ of the last term, integrate over \mathbf{r} of the δ -term, and obtain the expression,

$$\begin{aligned}
E_V &= - \int n(\mathbf{r}'') \mathbf{r}'' \cdot \nabla_{(r'')} \left[\right. \\
&\quad -2 \sum_{i,j} \frac{I^{ij}(\mathbf{r}'') f_j(\mathbf{r}'') f_i(\mathbf{r}'')}{2n(\mathbf{r}'')} \\
&\quad \left. -2 \sum_{i,j} \int_{r''}^\infty I^{ij}(r) f_j(r) \left\{ \frac{1}{n(r)} \left[\frac{\partial f_i}{\partial r} - \frac{f_i(r)}{2n^\sigma(r)} \frac{\partial n^\sigma(r)}{\partial r} \right] \right\} \right] dr \\
&\quad \left. \right] r'^2 \sin(\theta'') dr'' d\theta'' d\phi''. \tag{C.3}
\end{aligned}$$

We expand the last term and obtain (signs in first term are shown for emphasis)

$$\begin{aligned}
E_V &= + \int n(\mathbf{r}'') \mathbf{r}'' \cdot \nabla_{(r'')} \left[\sum_{i,j} \frac{I^{ij}(\mathbf{r}'') f_j(\mathbf{r}'') f_i(\mathbf{r}'')}{n(\mathbf{r}'')} \right] r'^2 \sin(\theta'') dr'' d\theta'' d\phi'' \\
&\quad -2 \int n(\mathbf{r}'') \mathbf{r}'' \cdot \sum_{i,j} \frac{I^{ij}(r'') f_j(r'')}{n(r'')} \frac{\partial f_i(r'')}{\partial r''} r'^2 \sin(\theta'') dr'' d\theta'' d\phi'' \\
&\quad + \int n(\mathbf{r}'') \mathbf{r}'' \cdot \sum_{i,j} \frac{I^{ij}(r'') f_j(r'') f_i(r'')}{n(r'')^2} \frac{\partial n(r'')}{\partial r''} r'^2 \sin(\theta'') dr'' d\theta'' d\phi''.
\end{aligned}$$

Evaluating the gradient in the first term (product rule) leads to the following contributions:

$$\begin{aligned}
E_V &= + \int n(\mathbf{r}'') \mathbf{r}'' \cdot \left[\sum_{i,j} \frac{f_j(\mathbf{r}'') f_i(\mathbf{r}'')}{n(\mathbf{r}'')} \nabla_{(\mathbf{r}'')} I^{ij}(\mathbf{r}'') \right] r''^2 \sin(\theta'') \, dr'' \, d\theta'' \, d\phi'' \\
&+ \underbrace{\int n(\mathbf{r}'') \mathbf{r}'' \cdot \left[\sum_{i,j} \frac{I^{ij}(\mathbf{r}'') f_i(\mathbf{r}'')}{n(\mathbf{r}'')} \frac{\partial f_j(\mathbf{r}'')}{\partial r''} \right]}_{A1} r''^2 \sin(\theta'') \, dr'' \, d\theta'' \, d\phi'' \\
&+ \underbrace{\int n(\mathbf{r}'') \mathbf{r}'' \cdot \left[\sum_{i,j} \frac{I^{ij}(\mathbf{r}'') f_j(\mathbf{r}'')}{n(\mathbf{r}'')} \frac{\partial f_i(\mathbf{r}'')}{\partial r''} \right]}_{A2} r''^2 \sin(\theta'') \, dr'' \, d\theta'' \, d\phi'' \\
&- \underbrace{\int n(\mathbf{r}'') \mathbf{r}'' \cdot \left[\sum_{i,j} \frac{I^{ij}(\mathbf{r}'') f_j(\mathbf{r}'') f_i(\mathbf{r}'')}{n(\mathbf{r}'')^2} \frac{\partial n(\mathbf{r}'')}{\partial r''} \right]}_B r''^2 \sin(\theta'') \, dr'' \, d\theta'' \, d\phi'' \\
&- 2 \underbrace{\int n(\mathbf{r}'') \mathbf{r}'' \cdot \sum_{i,j} \frac{I^{ij}(\mathbf{r}'') f_j(\mathbf{r}'')}{n(\mathbf{r}'')} \frac{\partial f_i(\mathbf{r}'')}{\partial r''}}_{-(A1+A2)} r''^2 \sin(\theta'') \, dr'' \, d\theta'' \, d\phi'' \\
&+ \underbrace{\int n(\mathbf{r}'') \mathbf{r}'' \cdot \sum_{i,j} \frac{I^{ij}(\mathbf{r}'') f_j(\mathbf{r}'') f_i(\mathbf{r}'')}{n(\mathbf{r}'')^2} \frac{\partial n(\mathbf{r}'')}{\partial r''}}_{-B} r''^2 \sin(\theta'') \, dr'' \, d\theta'' \, d\phi''
\end{aligned}$$

Finally,

$$\begin{aligned}
E_V &= + \int n(\mathbf{r}'') \left[\sum_{i,j} \frac{f_j(\mathbf{r}'') f_i(\mathbf{r}'')}{n(\mathbf{r}'')} \mathbf{r}'' \cdot \nabla_{(\mathbf{r}'')} I^{ij}(\mathbf{r}'') \right] r''^2 \sin(\theta'') \, dr'' \, d\theta'' \, d\phi'' \\
&= + \int \left[\sum_{i,j} f_j(\mathbf{r}'') f_i(\mathbf{r}'') \mathbf{r}'' \cdot \nabla_{(\mathbf{r}'')} \underbrace{\int \frac{f_i(\mathbf{r}') f_j(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}''|}}_{I^{ij}(\mathbf{r}'')} \right] r''^2 \sin(\theta'') \, dr'' \, d\theta'' \, d\phi''.
\end{aligned}$$

This integral has the form

$$\int \tilde{n}_j(\mathbf{r}) \mathbf{r} \cdot \nabla_{(\mathbf{r})} \int \frac{\tilde{n}_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r}' \quad \text{with } \tilde{n}_j(\mathbf{r}) = f_i(\mathbf{r}) f_j(\mathbf{r}) \quad (\text{C.4})$$

and is the analog of the Virial theorem of the Hartree term, in which case the last integral reduces to the expression,

$$E = -\frac{1}{2} \int \tilde{n}(\mathbf{r}) \int \frac{\tilde{n}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r}' \, d\mathbf{r}. \quad (\text{C.5})$$

We have succeeded in showing that, for spherical orbitals and a spherical density,

$$E_V = E_x \quad (\text{C.6})$$

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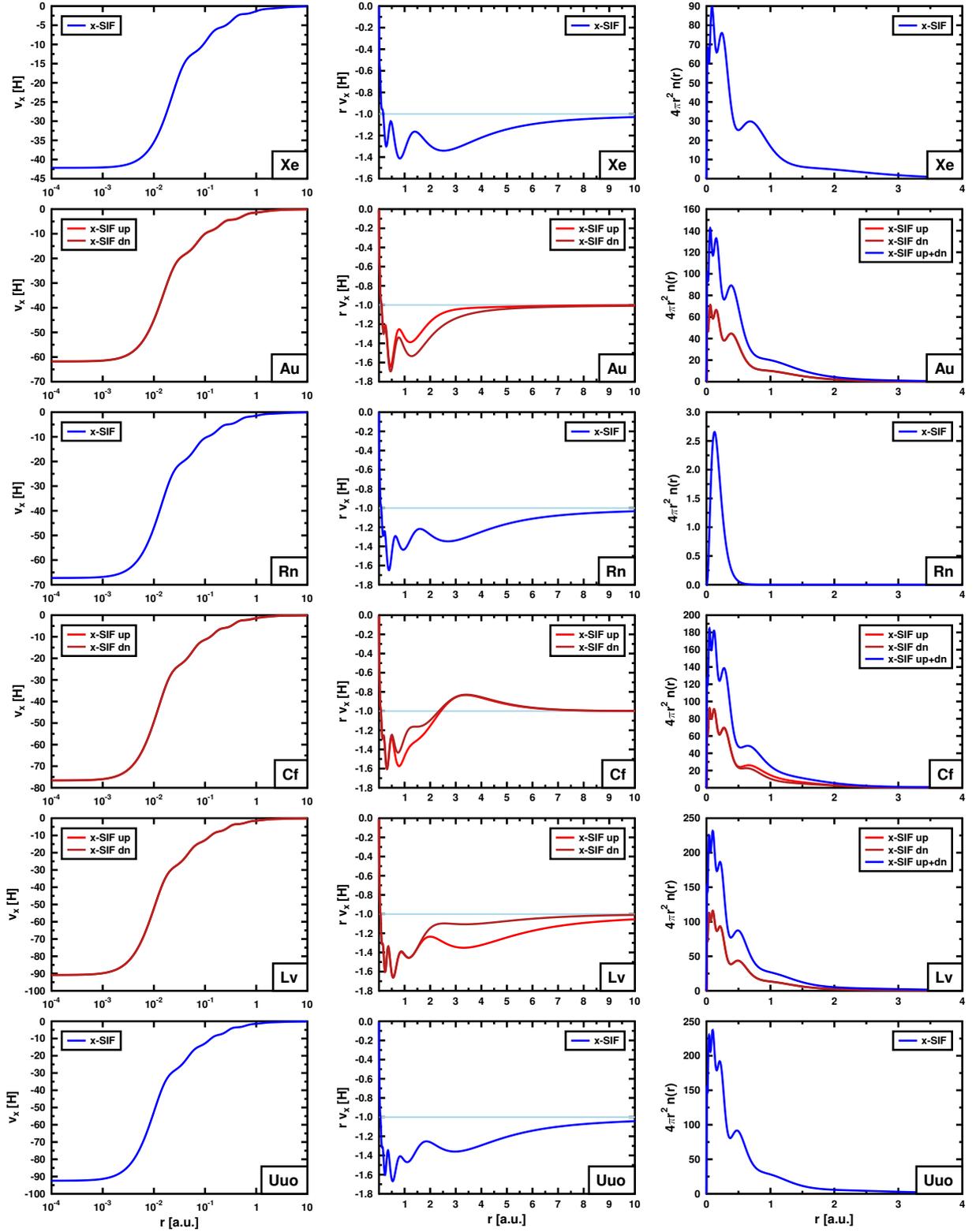


Figure C.2: Exchange potentials for Xenon, Gold, Radon, Californium, Livermorium and Ununoctium, and their corresponding (spin) densities, obtained through the SIF method in the exchange-only mode.

Z	symbol	configuration*	energy[H]	Z	symbol	configuration*	energy[H]
2	He	1s ²	-2.862	61	Pm	[Xe] 4f ⁵ 6s ²	-9655.029
3	Li	[He] 2s ¹	-7.432	62	Sm	[Xe] 4f ⁶ 6s ²	-10034.908
4	Be	[He] 2s ²	-14.571	63	Eu	[Xe] 4f ⁷ 6s ²	-10423.499
5	B	[He] 2s ² 2p ¹	-24.527	64	Gd	[Xe] 4f ⁷ 5d ¹ 6s ²	-10820.618
6	C	[He] 2s ² 2p ²	-37.687	65	Tb	[Xe] 4f ⁹ 6s ²	-11226.493
7	N	[He] 2s ² 2p ³	-54.401	66	Dy	[Xe] 4f ¹⁰ 6s ²	-11641.343
8	O	[He] 2s ² 2p ⁴	-74.809	67	Ho	[Xe] 4f ¹¹ 6s ²	-12065.175
9	F	[He] 2s ² 2p ⁵	-99.406	68	Er	[Xe] 4f ¹² 6s ²	-12498.063
10	Ne	[He] 2s ² 2p ⁶	-128.542	69	Tm	[Xe] 4f ¹³ 6s ²	-12940.111
11	Na	[Ne] 3s ¹	-161.852	70	Yb	[Xe] 4f ¹⁴ 6s ²	-13391.390
12	Mg	[Ne] 3s ²	-199.606	71	Lu	[Xe] 4f ¹⁴ 5d ¹ 6s ²	-13851.747
13	Al	[Ne] 3s ² 3p ¹	-241.868	72	Hf	[Xe] 4f ¹⁴ 5d ² 6s ²	-14321.185
14	Si	[Ne] 3s ² 3p ²	-288.845	73	Ta	[Xe] 4f ¹⁴ 5d ³ 6s ²	-14799.751
15	P	[Ne] 3s ² 3p ³	-340.709	74	W	[Xe] 4f ¹⁴ 5d ⁴ 6s ²	-15287.497
16	S	[Ne] 3s ² 3p ⁴	-397.495	75	Re	[Xe] 4f ¹⁴ 5d ⁵ 6s ²	-15784.488
17	Cl	[Ne] 3s ² 3p ⁵	-459.470	76	Os	[Xe] 4f ¹⁴ 5d ⁶ 6s ²	-16290.600
18	Ar	[Ne] 3s ² 3p ⁶	-526.804	77	Ir	[Xe] 4f ¹⁴ 5d ⁷ 6s ²	-16806.049
19	K	[Ar] 4s ¹	-599.150	78	Pt	[Xe] 4f ¹⁴ 5d ⁹ 6s ¹	-17331.014
20	Ca	[Ar] 4s ²	-676.743	79	Au	[Xe] 4f ¹⁴ 5d ¹⁰ 6s ¹	-17865.343
21	Sc	[Ar] 3d ¹ 4s ²	-759.718	80	Hg	[Xe] 4f ¹⁴ 5d ¹⁰ 6s ²	-18408.932
22	Ti	[Ar] 3d ² 4s ²	-848.375	81	Tl	[Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ¹	-18961.768
23	V	[Ar] 3d ³ 4s ²	-942.852	82	Pb	[Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ²	-19523.954
24	Cr	[Ar] 3d ⁵ 4s ¹	-1043.334	83	Bi	[Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ³	-20095.535
25	Mn	[Ar] 3d ⁵ 4s ²	-1149.848	84	Po	[Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁴	-20676.450
26	Fe	[Ar] 3d ⁶ 4s ²	-1262.425	85	At	[Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁵	-21266.831
27	Co	[Ar] 3d ⁷ 4s ²	-1381.376	86	Rn	[Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁶	-21866.721
28	Ni	[Ar] 3d ⁸ 4s ²	-1506.829	87	Fr	[Rn] 7s ¹	-22475.808
29	Cu	[Ar] 3d ¹⁰ 4s ¹	-1638.938	88	Ra	[Rn] 7s ²	-23094.254
30	Zn	[Ar] 3d ¹⁰ 4s ²	-1777.820	89	Ac	[Rn] 6d ¹ 7s ²	-23722.142
31	Ga	[Ar] 3d ¹⁰ 4s ² 4p ¹	-1923.235	90	Th	[Rn] 6d ² 7s ²	-24359.566
32	Ge	[Ar] 3d ¹⁰ 4s ² 4p ²	-2075.335	91	Pa	[Rn] 5f ² 6d ¹ 7s ²	-25007.026
33	As	[Ar] 3d ¹⁰ 4s ² 4p ³	-2234.215	92	U	[Rn] 5f ³ 6d ¹ 7s ²	-25664.233
34	Se	[Ar] 3d ¹⁰ 4s ² 4p ⁴	-2399.844	93	Np	[Rn] 5f ⁴ 6d ¹ 7s ²	-26331.349
35	Br	[Ar] 3d ¹⁰ 4s ² 4p ⁵	-2572.417	94	Pu	[Rn] 5f ⁶ 7s ²	-27008.668
36	Kr	[Ar] 3d ¹⁰ 4s ² 4p ⁶	-2752.030	95	Am	[Rn] 5f ⁷ 7s ²	-27695.837
37	Rb	[Kr] 5s ¹	-2938.331	96	Cm	[Rn] 5f ⁷ 6d ¹ 7s ²	-28392.720
38	Sr	[Kr] 5s ²	-3131.520	97	Bk	[Rn] 5f ⁸ 6d ¹ 7s ²	-29099.777
39	Y	[Kr] 4d ¹ 5s ²	-3331.657	98	Cf	[Rn] 5f ¹⁰ 7s ²	-29817.314
40	Zr	[Kr] 4d ² 5s ²	-3538.959	99	Es	[Rn] 5f ¹¹ 7s ²	-30544.862
41	Nb	[Kr] 4d ⁴ 5s ¹	-3753.569	100	Fm	[Rn] 5f ¹² 7s ²	-31282.686
42	Mo	[Kr] 4d ⁵ 5s ¹	-3975.520	101	Md	[Rn] 5f ¹³ 7s ²	-32030.861
43	Tc	[Kr] 4d ⁵ 5s ²	-4204.762	102	No	[Rn] 5f ¹⁴ 7s ²	-32789.438
44	Ru	[Kr] 4d ⁷ 5s ¹	-4441.495	103	Lr	[Rn] 5f ¹⁴ 6d ¹ 7s ²	-33557.879
45	Rh	[Kr] 4d ⁸ 5s ¹	-4685.835	104	Rf	[Rn] 5f ¹⁴ 6d ² 7s ²	-34336.545
46	Pd	[Kr] 4d ¹⁰	-4937.889	105	Db	[Rn] 5f ¹⁴ 6d ³ 7s ²	-35125.471
47	Ag	[Kr] 4d ¹⁰ 5s ¹	-5197.661	106	Sg	[Rn] 5f ¹⁴ 6d ⁴ 7s ²	-35924.695
48	Cd	[Kr] 4d ¹⁰ 5s ²	-5465.093	107	Bh	[Rn] 5f ¹⁴ 6d ⁵ 7s ²	-36734.266
49	In	[Kr] 4d ¹⁰ 5s ² 5p ¹	-5740.130	108	Hs	[Rn] 5f ¹⁴ 6d ⁶ 7s ²	-37554.059
50	Sn	[Kr] 4d ¹⁰ 5s ² 5p ²	-6022.894	109	Mt	[Rn] 5f ¹⁴ 6d ⁷ 7s ²	-38384.265
51	Sb	[Kr] 4d ¹⁰ 5s ² 5p ³	-6313.451	110	Ds	[Rn] 5f ¹⁴ 6d ⁸ 7s ²	-39224.917
52	Te	[Kr] 4d ¹⁰ 5s ² 5p ⁴	-6611.749	111	Rg	[Rn] 5f ¹⁴ 6d ⁹ 7s ²	-40076.053
53	I	[Kr] 4d ¹⁰ 5s ² 5p ⁵	-6917.945	112	Cn	[Rn] 5f ¹⁴ 6d ¹⁰ 7s ²	-40937.724
54	Xe	[Kr] 4d ¹⁰ 5s ² 5p ⁶	-7232.102	113	Uut	[Rn] 5f ¹⁴ 6d ¹⁰ 7s ² 7p ¹	-41809.464
55	Cs	[Xe] 6s ¹	-7553.896	114	Fl	[Rn] 5f ¹⁴ 6d ¹⁰ 7s ² 7p ²	-42691.589
56	Ba	[Xe] 6s ²	-7883.508	115	Uup	[Rn] 5f ¹⁴ 6d ¹⁰ 7s ² 7p ³	-43584.133
57	La	[Xe] 5d ¹ 6s ²	-8221.028	116	Lv	[Rn] 5f ¹⁴ 6d ¹⁰ 7s ² 7p ⁴	-44487.035
58	Ce	[Xe] 4f ¹ 5d ¹ 6s ²	-8566.808	117	Uus ¹⁷	[Rn] 5f ¹⁴ 6d ¹⁰ 7s ² 7p ⁵	-45400.409
59	Pr	[Xe] 4f ³ 6s ²	-8921.092	118	Uuo	[Rn] 5f ¹⁴ 6d ¹⁰ 7s ² 7p ⁶	-46324.291
60	Nd	[Xe] 4f ⁴ 6s ²	-9283.791				

* This is the configuration used in calculations. In some cases, particularly for higher Z elements, the configuration is assumed.

Table C.1: Energies and calculated configurations within the exchange-only mode throughout the periodic table.