# Ensemble interpretation of L(S)DA+*U*

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We propose an ensemble interpretation of the L(S)DA+*U* functional aiming at the construction of a well-defined rigorous scheme as a reference point for further investigations of the functional. An explicit ensemble state, which realizes the conventional L(S)DA+*U* interaction term proportional to the product of the orbital-occupation numbers, is presented. It cannot, however, represent the correct interaction in the general case as it produces spurious self-interaction. We propose to consider the interaction term as resulting from a variational problem and present a method for its solution. As a functional of orbital occupations the interaction term results in piecewise constant corrections to the orbital potentials. The double-counting term is treated as the value of the interaction term for a spherically symmetric atomic configuration. The resulting expression is related to the so-called atomic limit for the double-counting term. It completely cancels the isotropic part (corresponding to the parameter *U* of the Hubbard model) of the interaction term, so that only the anisotropic part responsible for the so-called orbital polarization correction remains.

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## I. INTRODUCTION

Density-functional theory is nowadays one of the most used methods for calculating properties of many-electron systems. Being in principle exact, the theory requires, however, approximations as the key ingredient of the theory—the exchange-correlation functional—is not known. The simplest approximate functional is the local (spin-) density approximation[1] [L(S)DA], which proves to be very successful for a wide variety of materials. Yet, it is well known that the approximation often fails to describe correctly the properties of systems with localized *d* or *f* electrons. The reason of the LDA failure is an inadequate description of the correlations. The L(S)DA+*U* method[2–6] represents a simple and successful correction scheme improving the description. The method is still the subject of intensive research.[7]

There are, however, some open questions concerning the approach. For example, the double-counting term is introduced on empirical grounds and the interaction term produces spurious self-interaction. In this paper we present an ensemble interpretation of L(S)DA+*U*, which allows to consider the double-counting and interaction terms on the same grounds and relies only on a good description of spherically symmetric states by a basic approximation such as L(S)DA. The developed method delivers in general an anisotropic correction different from that obtained in the conventional formulation of L(S)DA+*U* coinciding with the latter in the case of integer orbital-occupation numbers.

The paper is organized as follows. Section II reviews the basics of the rotationally invariant formulation of L(S)DA +*U*. A derivation of the double-counting term as an energy of the spherically symmetrized state is given in Sec. III. Side by side with the well-known LSDA expressions those for LDA are derived. It is shown that the so-called atomic limit (AL) term represents a certain ensemble average of the open-shell atomic state. Section IV presents an ensemble state, which realizes the conventional interaction term proportional to the product of the orbital-occupation numbers. The variational interaction term minimizing the electron-electron interaction for a given occupation of open-shell orbitals is presented in Sec. V. The term is free of spurious self-interaction inherit in the conventional interaction term. A practically realizable scheme for computing the interaction term is developed. In Sec. VI the double-counting term is discussed again in the framework of the obtained results. The last two sections present application examples and concluding remarks, respectively. Proofs of some important mathematical statements are given in the appendices.

Though the paper is restricted to the context of L(S)DA +*U*, the proposed method can be applied for calculating corrections to any approximation delivering reliable values for the occupation of local orbitals.

## II. ROTATIONALLY INVARIANT L(S)DA+*U*

The essence of the L(S)DA+*U* approach is in explicitly treating the intra-atomic electron-electron interaction as a functional of orbital occupations in an open shell

$$E^{\mathrm{L(S)DA}+U}[\rho,\{\phi\}] = E^{\mathrm{L(S)DA}}[\rho] + E_{ee}(\hat{n}) - E_{\mathrm{dc}}^{\mathrm{L(S)DA}}(\hat{n}), \quad (1)$$

where the orbital-occupation matrix $\hat{n}[\rho,\{\phi\}]$ is determined by the given set of open-shell orbitals $\{\phi\}$ and the electron density $\rho$. $E_{\mathrm{dc}}$ is the double-counting term assumed to take care of the averaged part of the interaction already present in L(S)DA.

The rotationally invariant form of the interaction term[6] reads in the most general form as

$$E_{ee} = \frac{1}{2}\sum_{\mu\mu'\lambda\lambda'} n_{\mu\lambda} n_{\mu'\lambda'} W_{\mu\lambda;\mu'\lambda'} \quad (2)$$

with

$$W_{\mu\lambda;\mu'\lambda'} = \langle \lambda\lambda' | \tilde{w} | \mu\mu' \rangle - \langle \lambda'\lambda | \tilde{w} | \mu\mu' \rangle = U_{\mu\lambda;\mu'\lambda'} - J_{\mu\lambda;\mu'\lambda'},$$

where $\mu$ is a set of quantum numbers characterizing the orbital $\phi_\mu$ used also as a shortening for the orbital, $\tilde{w}$ is a

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screened electron-electron interaction, and $n_{\mu\lambda}$ are the elements of the occupation matrix defined by

$$n_{\mu\lambda}[\rho] = \sum_i \langle \mu|\psi_i\rangle p_i \langle \psi_i|\lambda\rangle,$$

where $\psi_i$ and $p_i$ are the Kohn-Sham orbitals and their occupation numbers, respectively.[8]

The term $E_U \equiv E_{ee} - E_{\rm dc}$ in the expression (1) results in an additional term in the Hamiltonian

$$\hat{H}_U = \sum_{\mu\lambda} |\lambda\rangle v_{\lambda\mu} \langle\mu|$$

with

$$v_{\lambda\mu} \equiv \frac{\partial E_U}{\partial n_{\mu\lambda}} = \frac{\partial E_{ee}}{\partial n_{\mu\lambda}} - \frac{\partial E_{\rm dc}}{\partial n_{\mu\lambda}} \equiv v^{ee}_{\lambda\mu} - v^{\rm dc}_{\lambda\mu}. \tag{3}$$

The term "rotationally invariant" for expression (2) is not most appropriate as it is, in fact, invariant with respect to any unitary transformation $\phi_\mu = \Sigma_m T_{m\mu}\phi_m$ acting in the subspace of the local orbitals, provided that the double-counting term $E_{\rm dc}$ is invariant under such a transformation.[9] Particularly, it is always possible to transform the occupation matrix to the diagonal form. It is not convenient to carry out the diagonalization of the occupation matrix in practical computations as it complicates the calculation of the interaction matrix elements, which is most easily performed choosing spherical harmonics as local orbitals. However the diagonal representation is very suitable for analysis and is used in what follows. We shall refer to the orbitals corresponding to the diagonal representation as *natural open-shell orbitals*.

The general expression (2) reads in the diagonal representation as

$$E_{ee} = \frac{1}{2}\sum_{\mu\mu'} n_\mu n_{\mu'} W_{\mu\mu'} \tag{4}$$

with

$$W_{\mu\mu'} = \langle \mu\mu'|\tilde{w}|\mu\mu'\rangle - \langle \mu'\mu|\tilde{w}|\mu\mu'\rangle = U_{\mu\mu'} - J_{\mu\mu'}.$$

If, as is usually the case, the Kohn-Sham potential does not mix the spin and the Kohn-Sham orbitals $\psi_i$ are therefore pure spin states, one can restrict the orbital transformations to the spin subspaces and consider the matrices $n^\sigma_m$, where $m$ is a collection of quantum numbers describing the space part of the local orbitals. In this case it is convenient to rewrite expression (4) as

$$E_{ee} = \frac{1}{2}\sum_{mm'\sigma\sigma'} n^\sigma_m n^{\sigma'}_{m'} W^{\sigma\sigma'}_{mm'}$$

with

$$W^{\sigma\sigma'}_{mm'} = U^{\sigma\sigma'}_{mm'} - J^{\sigma\sigma'}_{mm'}\delta_{\sigma\sigma'},$$

where we assume in a general case that the majority and minority spin subshells may have different radial parts of orbitals.

## III. DOUBLE-COUNTING TERM

The main source of uncertainty in the L(S)DA+$U$ approach is the double-counting term responsible for the part of the on-site correlations already present in L(S)DA. The usual way to arrive at the expression is the assumption that L(S)DA works rather well for spherically symmetric atomic densities (in the LSDA case spherical symmetry of both spin densities is implied). There are two common ways to construct a spherically symmetric counterpart for a given configuration. The first way is the equal—in general fractional—occupation of all open- (spin-) shell orbitals. The other—physically more appropriate—way is the construction of an ensemble state choosing the weights of many-electron pure states spanning the Hilbert subspace corresponding to the open shell in such a way that the resulting electron density is spherically symmetric.

### A. Fractional orbital occupation

In the assumption of equal orbital occupation the expression for the double-counting term in the LSDA case reads

$$E^{\rm MF-LSDA}_{\rm dc} = \frac{1}{2}\sum_{mm'\sigma\sigma'} \frac{N_\sigma}{M_\sigma}\frac{N_{\sigma'}}{M_{\sigma'}}(U^{\sigma\sigma'}_{mm'} - J^{\sigma\sigma'}_{mm'}\delta_{\sigma\sigma'})$$
$$= \frac{1}{2}\left[2U_{\sigma\bar{\sigma}}N_\sigma N_{\bar{\sigma}} + \sum_\sigma (U_{\sigma\sigma} - J_{\sigma\sigma})N^2_\sigma\left(1 - \frac{1}{M_\sigma}\right)\right],$$

where $N_\sigma$ and $M_\sigma$ are the numbers of electrons and orbitals in a $\sigma$ spin subshell and $U_{\sigma\sigma'}$ and $J_{\sigma\sigma}$ are defined by the identities

$$\sum_m U^{\sigma\sigma'}_{mm'} = M_\sigma U_{\sigma\sigma'}, \tag{5}$$

$$\sum_m U^{\sigma\sigma}_{mm'} - J^{\sigma\sigma}_{mm'} = (M_\sigma - 1)(U_{\sigma\sigma} - J_{\sigma\sigma}). \tag{6}$$

Note that the sum on the left-hand side of the Eqs. (5) and (6) does not depend on the index $m'$.[4,10]

Under the assumption of the same radial part of spin-up and spin-down orbitals ($U_{\sigma\sigma'} \equiv U, J_{\sigma\sigma} \equiv J$) the expression

$$E^{\rm MF-LSDA}_{\rm dc} = UN_\sigma N_{\bar{\sigma}} + \frac{1}{2}(U-J)\sum_\sigma N^2_\sigma\left(1 - \frac{1}{M_\sigma}\right)$$

can be readily recognized as the so-called around mean-field double-counting term.[2,3,7]

In the LDA case we shall assume $N_\sigma = N_{\bar{\sigma}} = N/2$ and $M_\sigma = M_{\bar{\sigma}} = M/2$ and arrive to

$$E^{\rm MF-LDA}_{\rm dc} = \frac{1}{2}\left[UN^2\left(1 - \frac{1}{M}\right) - JN^2\left(\frac{1}{2} - \frac{1}{M}\right)\right]$$
$$= \frac{1}{2}(U - J^*)N^2\left(1 - \frac{1}{M}\right), \tag{7}$$

where we introduce

$$J^* = J\frac{M-2}{2(M-1)} = J\frac{2l}{4l+1} \tag{8}$$

with $l$ being the orbital quantum number of the open shell, so that $M=2(2l+1)$.

Note that $J^*$ is the value of the exchange integral used in the theory of atomic spectra,[11] whereas $J$ introduced in Ref. 3 is a renormalized value taking into account the part of the exchange interaction explicitly present in LSDA.

### B. Ensemble state

The simplest way to construct a spherically symmetric $N$-electron ensemble state, where $N$ is an integer number, is to choose equal weights $\omega$ for all pure states $\Psi$ forming a complete basis set spanning the $N$-electron configurations of the open shell

$$\Omega_0 = \sum_i |\Psi_i\rangle\omega\langle\Psi_i|; \quad \sum_i \omega = 1. \tag{9}$$

Such a state is further referred to as spherically symmetric *homogeneous ensemble state* (a convex combination of pure states having the same number of electrons).

Let $\Phi$ be some arbitrary complete basis set spanning the same configuration subspace. For the expectation value of an operator $\hat{O}$ acting onto an ensemble state in Eq. (9) one obtains

$$\langle\hat{O}\rangle_{\Omega_0} = \mathrm{Tr}[\hat{O}\Omega_0] = \omega\sum_i \langle\Psi_i|\hat{O}|\Psi_i\rangle = \omega\sum_i \langle\Phi_i|\hat{O}|\Phi_i\rangle,$$

the last equality holding due to the fact that the trace of an operator does not depend on its representation. The result shows that any complete basis set can be used for representing the ensemble state in Eq. (9). In our case it is convenient to choose Slater determinants of the open-shell orbitals as such a basis set.

First we consider the LSDA case with integer numbers of electrons $N_\sigma$ and $N_{\bar\sigma}$ in each spin shell. There are $\binom{M_\sigma}{N_\sigma}\binom{M_{\bar\sigma}}{N_{\bar\sigma}}$ ways to place the electrons. If one fixes two electrons the number of ways to place the rest is either $\binom{M_\sigma-2}{N_\sigma-2}\binom{M_{\bar\sigma}}{N_{\bar\sigma}}$ if both electrons belong to the same $\sigma$ spin shell or $\binom{M_\sigma-1}{N_\sigma-1}\binom{M_{\bar\sigma}-1}{N_{\bar\sigma}-1}$ if they belong to different spin shells and one arrives at the following expression for the double-counting term

$$E_{\mathrm{dc}}^{\mathrm{AL-LSDA}} = \frac{1}{2}\left[\binom{M_\sigma}{N_\sigma}\binom{M_{\bar\sigma}}{N_{\bar\sigma}}\right]^{-1}\sum_{mm'\sigma}\left\{\binom{M_\sigma-1}{N_\sigma-1}\binom{M_{\bar\sigma}-1}{N_{\bar\sigma}-1}U_{mm'}^{\sigma\bar\sigma} + \binom{M_\sigma-2}{N_\sigma-2}\binom{M_{\bar\sigma}}{N_{\bar\sigma}}(U_{mm'}^{\sigma\sigma}-J_{mm'}^{\sigma\sigma})\right\}$$

$$= \frac{1}{2}\sum_{mm'}\left\{2\frac{N_\sigma}{M_\sigma}\frac{N_{\bar\sigma}}{M_{\bar\sigma}}U_{mm'}^{\sigma\bar\sigma} + \sum_\sigma\frac{N_\sigma(N_\sigma-1)}{M_\sigma(M_\sigma-1)}(U_{mm'}^{\sigma\sigma}-J_{mm'}^{\sigma\sigma})\right\} = \frac{1}{2}\left[2U_{\sigma\bar\sigma}N_\sigma N_{\bar\sigma} + \sum_\sigma (U_{\sigma\sigma}-J_{\sigma\sigma})N_\sigma(N_\sigma-1)\right],$$

where $U_{\sigma\sigma'}$ and $J_{\sigma\sigma}$ are defined by identities in Eqs. (5) and (6).

Under the assumption of the same radial part of the spin-up and spin-down orbitals the expression

$$E_{\mathrm{dc}}^{\mathrm{AL-LSDA}} = UN_\sigma N_{\bar\sigma} + \frac{1}{2}(U-J)\sum_\sigma N_\sigma(N_\sigma-1) \tag{10}$$

can be readily recognized as the so-called AL double-counting term.[4,5,7]

In the LDA case we shall replace the products such as $\binom{M_\sigma}{N_\sigma}\binom{M_{\bar\sigma}}{N_{\bar\sigma}}$ by $\binom{M_\sigma+M_{\bar\sigma}}{N_\sigma+N_{\bar\sigma}} \equiv \binom{M}{N}$ and in the same line as above obtain the expression

$$E_{\mathrm{dc}}^{\mathrm{AL-LDA}} = \frac{1}{2}(U-J^*)N(N-1), \tag{11}$$

with $J^*$ as defined by Eq. (8). Note that the expression is different from that given in Ref. 5

$$\frac{1}{2}UN(N-1) - \frac{1}{4}JN(N-2),$$

which can be obtained by substitution of $N_\sigma=N_{\bar\sigma}=N/2$ into Eq. (10).

It is easy to check that the occupation numbers of all orbitals in the open- (spin-) shell of the spherically symmetric homogeneous ensemble state are equal. Actually there are $\binom{M_{(\sigma)}-1}{N_{(\sigma)}-1}$ determinantal states containing the given orbital (this is the number of ways to place the other electrons in the shell). Dividing the number by the overall number of determinantal states $\binom{M_{(\sigma)}}{N_{(\sigma)}}$ one obtains for the orbital occupation the same number $N_{(\sigma)}/M_{(\sigma)}$ as in the fractional occupation method described in the previous Sec. III A.

In the conventional L(S)DA+$U$ method the expressions (10) and (11) are used for fractional electron numbers as well.[4,5] Being quite successful the approach is, however, purely empirical. As shown below this expression does not correspond to any possible ensemble state.

In the LDA case the simplest spherically symmetric ensemble state with a fractional number of electrons $N=\underline{N}+\bar{n}$ $(0\le\bar{n}<1)$ is just a convex mixture of the homogeneous states with the nearest smaller and larger integer numbers of electrons

$$\tilde{\Omega}_0[N] = \underline{n}\Omega_0[\underline{N}] + \bar{n}\Omega_0[\bar{N}],$$

where $\underline{N}$ is the floor of $N$ (the largest integer smaller than or equal to $N$), $\bar{N}=\underline{N}+1$ and $\underline{n}=1-\bar{n}$. For the corresponding

energy one obtains (hereafter we drop the abbreviation "AL" specifying the double-counting term)

$$\tilde{E}_{\rm dc}^{\rm LDA}(N) = \underline{n} E_{\rm dc}^{\rm LDA}(\underline{N}) + \bar{n} E_{\rm dc}^{\rm LDA}(\bar{N}),$$

which after substitution of expression (12) reads

$$\tilde{E}_{\rm dc}^{\rm LDA}(N) = \frac{1}{2}(U - J^*)[N(N-1) + \bar{n}\underline{n}]. \tag{12}$$

The LSDA case is less obvious as expression (10) depends on two numbers $N_\sigma$ and $N_{\bar{\sigma}}$. A closer look leads one to the physically plausible idea of considering the "fractional number" extension as the lowest possible energy deliverable by a convex combination of spherically symmetric homogeneous ensemble states. The LDA expression (12) is already in the required form. In the LSDA case it reads (details can be found in the Appendix A)

$$\tilde{E}_{\rm dc}^{\rm LSDA}(N_\sigma, N_{\bar{\sigma}}) = U[N_\sigma N_{\bar{\sigma}} - \mathcal{F}(\bar{n}_\sigma, \bar{n}_{\bar{\sigma}})] + \frac{1}{2}(U - J)\sum_\sigma [N_\sigma(N_\sigma - 1) + \bar{n}_\sigma \underline{n}_\sigma], \tag{13}$$

where

$$\mathcal{F}(\bar{n}_\sigma, \bar{n}_{\bar{\sigma}}) = \begin{cases} \bar{n}_\sigma \bar{n}_{\bar{\sigma}}, & \bar{n}_\sigma + \bar{n}_{\bar{\sigma}} \le 1 \\ \underline{n}_\sigma \underline{n}_{\bar{\sigma}}, & \underline{n}_\sigma + \underline{n}_{\bar{\sigma}} \le 1 \end{cases}.$$

Note that the conventional LDA expression (11) gives for any fractional electron number $N$ an energy smaller than that of Eq. (12). As the latter expression represents the lowest possible energy derivable from an ensemble of spherically symmetric homogeneous states, it follows that there exists no such ensemble state corresponding to expression (11). The same is true in the LSDA case for a considerable part of the $(N_\sigma, N_{\bar{\sigma}})$ domain.

Up to this point our procedure for dealing with fractional electron numbers still needs a justification. Later we present a more rigorous way of treating the double-counting term.

## IV. CONVENTIONAL INTERACTION TERM

It is an interesting question as to whether expression (4) represents a possible interaction energy of an atomic (possibly ensemble) state. The answer to the question is affirmative and we present below the construction of the state.

Consider an ensemble state of an atom with an open shell consisting of $M$ orbitals whose occupation is subject to the condition $0 \le n_i \le 1$, and introduce a function

$$\pi_\mu(\boldsymbol{x}) = \pi_\mu(x_1, x_2, \ldots, x_M) = \prod_{i=1}^{M} x_i^{\mu_i}(1 - x_i)^{1-\mu_i}; \quad 0 \le x \le 1, \tag{14}$$

where the index $\mu$ is a *binary vector* (a vector whose components are either 0 or 1) of dimension $M$. Sometimes it is convenient to write the index as $\{k\}$, where $k$ is a subset of indices $[1, \ldots, M]$ of dimension $K$: $\{k_1 k_2 \ldots k_K\}$ meaning that $\mu_{k_1} = \mu_{k_2} = \cdots = \mu_{k_K} = 1$ and the other $\mu_i$ are 0.

It is easy to check (see Appendix B for details) that

$$\sum_\mu^{\lambda \in \mu} \pi_\mu(\boldsymbol{x}) = \boldsymbol{x}^{\boldsymbol{\lambda}},$$

where $\lambda \in \mu$ means $\mu_i = 1$ if $\lambda_i = 1$, and $\boldsymbol{x}^{\boldsymbol{\lambda}}$ means $\Pi_i x_i^{\lambda_i}$.

Consider now the ensemble state

$$\Pi(\boldsymbol{n}) = \sum_\mu |\Phi_\mu\rangle \pi_\mu(\boldsymbol{n}) \langle \Phi_\mu|, \tag{15}$$

where the sum runs over all possible $2^M$ binary combinations $\mu$, $\boldsymbol{n} = (n_1, n_2, \ldots, n_M)$ is the set (vector) of the orbital-occupation numbers and $\Phi_\mu$ is the determinantal state with orbitals whose index $\mu_i$ is equal to 1 being present. The vacuum state $\Phi_0$ is included on equal ground in the ensemble state.

The state in Eq. (15) realizes the required interaction in Eq. (4). Actually as follows from the definition in Eq. (14)

$$0 \le \pi_\mu(\boldsymbol{n}) \le 1; \quad \sum_\mu \pi_\mu(\boldsymbol{n}) = 1,$$

so that $\Pi$ is an allowed ensemble state with correct orbital-occupation numbers

$$\sum_\mu^{\phi_i \in \Phi_\mu} \pi_\mu(\boldsymbol{n}) = \sum_\mu^{\{i\} \in \mu} \pi_\mu(\boldsymbol{n}) = n_i$$

and the interaction terms

$$W_{ij} \sum_\mu^{\{\phi_i, \phi_j\} \in \Phi_\mu} \pi_\mu(\boldsymbol{n}) = W_{ij} \sum_\mu^{\{ij\} \in \mu} \pi_\mu(\boldsymbol{n}) = n_i n_j W_{ij},$$

where we assumed that the pair interaction $W_{ij}$ is identical for all determinantal states $\Phi_\mu$.

## V. VARIATIONAL INTERACTION TERM

Being very simple the conventional interaction term in Eq. (4) corresponds to physical reality only if at least one of two involved orbital-occupation numbers $n_i$ is an integer (i.e., 0 or 1). If it is not the case it produces spurious self-interaction. Consider an example of one electron spread over two orbitals with equal occupation $\frac{1}{2}$. It means that the electron oscillates between the orbitals and the state can be represented as an ensemble of two determinantal states each having the electron fixed in the corresponding orbital, which produces no electron-electron interaction. The term in Eq. (4) is, however, not 0 but $\frac{1}{8} W_{ij}$.

We propose to cure the problem by defining the "real" interaction as resulting from the minimization of the energy of a general ensemble state

$$\Omega = \sum_\mu |\Phi_\mu\rangle \omega_\mu \langle \Phi_\mu|; \quad 0 \le \omega_\mu \le 1; \quad \sum_\mu \omega_\mu = 1,$$

where $\Phi_\mu$ are determinantal states introduced in the previous section, for given orbital occupations $n_i$

$$E_{ee}(\boldsymbol{n}) = \inf_{\omega_\mu} \left\{ \sum_\mu \omega_\mu \mathcal{E}_\mu \,\middle|\, 0 \le \omega_\mu,\ \sum_\mu \omega_\mu = 1,\ \sum_\mu^{\{i\}\in\mu} \omega_\mu = n_i \right\}, \tag{16}$$

where

$$\mathcal{E}_\mu = \frac{1}{2} \sum_{ij} \mu_i \mu_j W_{ij} \tag{17}$$

is the energy of the state $\Phi_\mu$.

The state in Eq. (15) is a representative of all ensemble states with the interaction energy expressible as $E_\Pi = \frac{1}{2}\Sigma_{ij} n_i n_j W_{ij}$. Therefore its energy can be viewed as an upper bound for the functional Eq. (16)

$$E_{ee}(\boldsymbol{n}) \le E_\Pi(\boldsymbol{n}).$$

The bound is achieved when $\boldsymbol{n}$ is a binary vector.

As the minimized functional Eq. (16) is linear it takes the extreme values at the vertices of the polytope formed by intersection of the $(2^M - M - 1)$-dimensional plane specified by equations $\Sigma_\mu \omega_\mu = 1$ and $\Sigma_\mu^{i\in\mu} \omega_\mu = n_i$ $(i = 1, \ldots, M)$ with the polyhedral cone specified by $2^M$ inequalities $0 \le \omega_\mu$. One finds the vertices in the following way. Construct a $(M+1) \times 2^M$ rectangular matrix with rows representing the two last side conditions of Eq. (16)

$$\begin{pmatrix} 1 & 1 & 1 & 1 & \cdots & 1 & 1 & 1 & 1 \\ 0 & 1 & 0 & 1 & \cdots & 0 & 1 & 0 & 1 \\ 0 & 0 & 1 & 1 & \cdots & 0 & 0 & 1 & 1 \\ & & & & \cdots & & & & \\ 0 & 0 & 0 & 0 & \cdots & 1 & 1 & 1 & 1 \end{pmatrix}, \tag{18}$$

so that the last $M$ elements of each column encode the value of $\mu$. Pick up $M+1$ columns of the matrix to build a $(M+1) \times (M+1)$ square matrix representing a case with all $\omega_\mu$ but the chosen ones $\boldsymbol{\mu} = (\mu^0, \mu^1, \ldots, \mu^M)$ being 0. We shall refer to the inverse of the matrix (if it exists) as a $V$ matrix. The $V$ matrix multiplied from the right by column-vector $\tilde{\boldsymbol{n}} = (1, n_1, n_2, \ldots n_M)$

$$\boldsymbol{\omega}^{\boldsymbol{\mu}} = V^{\boldsymbol{\mu}} \cdot \tilde{\boldsymbol{n}}$$

is the vertex in question if all $M+1$ components of $\boldsymbol{\omega}^{\boldsymbol{\mu}}$ are non-negative. It remains to check which of the $\boldsymbol{\mu}$ vertices minimizes the functional Eq. (16). Introducing the row-vector $\mathcal{E}^{\boldsymbol{\mu}} = (\mathcal{E}_0^{\boldsymbol{\mu}}, \mathcal{E}_1^{\boldsymbol{\mu}}, \ldots, \mathcal{E}_M^{\boldsymbol{\mu}}) \equiv (\mathcal{E}_{\mu^0}, \mathcal{E}_{\mu^1}, \ldots, \mathcal{E}_{\mu^M})$ the energy expression can be written as

$$E_{\boldsymbol{\mu}}(\boldsymbol{n}) = \mathcal{E}^{\boldsymbol{\mu}} \cdot \boldsymbol{\omega}^{\boldsymbol{\mu}} = \boldsymbol{v}^{\boldsymbol{\mu}} \cdot \tilde{\boldsymbol{n}} = v_0^{\boldsymbol{\mu}} + \sum_{i=1}^{M} v_i^{\boldsymbol{\mu}} n_i, \tag{19}$$

the components of the vector

$$\boldsymbol{v}^{\boldsymbol{\mu}} = \mathcal{E}^{\boldsymbol{\mu}} \cdot V^{\boldsymbol{\mu}} \tag{20}$$

representing (for $i \neq 0$) the one-particle potentials in Eq. (3).

The described algorithm being, in principle, simple is, however, computationally intractable as it requires treatment of $\binom{2^M}{M+1}$ matrices. The huge number does not allow to carry out the brute force procedure for the practically important cases $M = 10$ and 14 ($d$ and $f$ shells, respectively).

To proceed further it is helpful to observe that the main result achieved above is a transformation of the $2^M$-dimensional problem in $\omega$ space into an $M$-dimensional one in $n$ space, where the determinantal states are represented by vertices of a $(0,1)^M$ cube. The $V$ matrices represent the whole variety of simplices inscribed in the cube. Any row of the $V$ matrix determines the equation of a hyperplane forming a face of the corresponding simplex, the normal of the hyperplane being directed inside the simplex. The geometrical meaning of the weights $\omega_i^{\boldsymbol{\mu}}$ is simple: it is the signed ratio of the distance between the point $\boldsymbol{n}$ and the $i$th hyperface of the $\boldsymbol{\mu}$ simplex to the distance between this hyperface and the opposite ($i$th) vertex, the sign of the ratio being positive if the point $\boldsymbol{n}$ and the $i$th vertex lie in the same half space with respect to the $i$th hyperface and negative in the opposite case. The weights are well known as *barycentric coordinates*. They are all non-negative only inside the corresponding simplex, which can be seen as a domain of homogeneous linear interpolation (convex combination) of the energies at its vertices.

Let us consider the energy as an additional $(M+1)$th coordinate. We shall refer to the point set formed by vertices upon adding the energy coordinate as the *lifted point configuration*. Any nondegenerate lifted simplex determines an $M$-dimensional plane in the considered $(M+1)$-dimensional space. The plane forms a facet of the *lower convex hull* of energy if no vertex of the lifted cube is in the lower (with respect to the energy coordinate) open half space determined by the plane.

As the lifted simplices represent the whole variety of planes spanned by the vertices of the lifted cube every facet of the lower convex hull lies in a plane determined by some simplex, any such simplex delivering the lowest energy attainable by a convex combination of vertex energies. Thus our problem is essentially reduced to finding the simplices forming the lower convex hull of the lifted occupation cube. After the simplices are found their projection onto the original $M$-dimensional space (i.e., elimination of the energy coordinate) represents a partition of the occupation cube into a disjoint union of simplices, the latter being further referred to as *minimizing* ones. Such a partition is known as *regular triangulation*.[12] Given the triangulation, it suffices to find the minimizing simplex containing the point $\boldsymbol{n}$ and apply Eq. (19) to obtain the energy minimizing the functional Eq. (16). Note that the effective potentials in Eq. (20) are piecewise constant having possible jumps at the boundaries of minimizing simplices.

The achieved simplification is dramatic, as any point in a general position is contained in a single minimizing simplex and the number of the simplices does not exceed $M!$, which is several orders of magnitude less than $\binom{2^M}{M+1}$ even for small values of $M$. In fact the lifting function Eq. (17) admits a regular triangulation of the cube into precisely $M!$ unimodular simplices.

There are plenty of effective algorithms for finding the convex hull of a given point set in a space of arbitrary dimension as, for example, the Quickhull algorithm.[13] For our specific point set (lifted cube) we, however, applied another way of finding the minimizing simplices using the fact that

any edge of such a simplex is a *leading diagonal* (ld) of the cube (the body diagonal of some cube face having the smallest value of the sum of the vertex energies). Details can be found in the Appendix C. Given the complete set of ld's the minimizing simplices can be identified in the following way. Choose a cube vertex and determine all ld's originating from this vertex. For every $M$-subset of these diagonals, check if all pairs of the opposite vertices are connected by ld. If it is the case check if no vertex of the lifted cube is below the plane determined by the resulting simplex. The efficiency of the method is justified *a posteriori* by the fact that the number of simplices satisfying the "edge criterion" does not much exceed the number of minimizing simplices. In the three-dimensional case the criterion appears to be even sufficient.[14]

## VI. DOUBLE-COUNTING TERM AGAIN

The main assumption of the interpretation being developed is a good description of the spherically symmetric ensemble states by the basic approximation (LDA or LSDA). To be consistent with the variational treatment of the interaction term we propose to define the double-counting term as

$$E_{\mathrm{dc}}^{\mathrm{L(S)DA}}(\boldsymbol{n}) = \inf_{\omega_\mu}\left\{ \sum_\mu \omega_\mu \mathcal{E}_\mu \,\middle|\, 0 \le \omega_\mu,\ \sum_\mu \omega_\mu = 1,\ \sum_\mu^{\{i\}\in\mu} \omega_\mu = \frac{N_{(\sigma_i)}}{M_{(\sigma_i)}} \right\}, \tag{21}$$

where the symbols in parentheses refer to the LSDA case, $\sigma_i$ is the spin projection of the orbital $i$ (pure spin character of orbitals is assumed), $N_{(\sigma_i)}=\sum_k^{(\sigma_k=\sigma_i)} n_k$ and $M_{(\sigma_i)}$ are the number of electrons and orbitals in the (spin) shell, respectively. The last side condition in Eq. (21) ensures that the variation is performed over the domain of spherically symmetric states. For such states the overall correction $E_{ee}-E_{\mathrm{dc}}$ is, by the construction, zero.

The variation domain in Eq. (21) is wider than that one used deriving Eqs. (12) and (13) as combinations of spherically asymmetric homogeneous ensemble states are allowed. Therefore

$$E_{\mathrm{dc}} \le \tilde{E}_{\mathrm{dc}}.$$

The expression (21) can be viewed as that for the interaction term in Eq. (16) estimated at the spherically symmetric counterpart of the given configuration. Geometrically the counterpart is represented in the LDA case by the orthogonal projection of the given point of the occupation cube onto the body diagonal connecting the "0" $(0,\ldots,0)$ and "1" $(1,\ldots,1)$ vertices. In the LSDA case the projection is performed onto the two-dimensional plane spanned by "0",

$$(\underbrace{1,\ldots,1}_{M_\sigma},\underbrace{0,\ldots,0}_{M_{\bar{\sigma}}})$$

and

$$(\underbrace{0,\ldots,0}_{M_\sigma},\underbrace{1,\ldots,1}_{M_{\bar{\sigma}}})$$

vertices.

The energy at the projection point can be determined by Eq. (19), which in this case reads

$$E_{\mathrm{dc}}^{\mathrm{LDA}} = v_0^{\boldsymbol{\mu}} + \frac{N}{M}\sum_{i=1}^{M} v_i^{\boldsymbol{\mu}}; \quad E_{\mathrm{dc}}^{\mathrm{LSDA}} = v_0^{\boldsymbol{\mu}} + \sum_\sigma \frac{N_\sigma}{M_\sigma}\sum_{i_\sigma=1}^{M_\sigma} v_{i_\sigma}^{\boldsymbol{\mu}},$$

where $\boldsymbol{\mu}$ denotes the minimizing simplex containing the point.

Applying this projection procedure onto the case of the conventional interaction term in Eq. (4) one easily obtains that its double-counting counterpart is the fractional occupation average expression (7) as was initially suggested in Refs. 2 and 3.

## VII. EXAMPLES

In what follows we refer to the proposed correction to L(S)DA functional as "+$V$" reflecting the fact that the energy is a piecewise linear functional of occupation numbers. The angular part of the natural open-shell orbitals is assumed to be described by standard (complex) spherical harmonics. For simplicity we consider only the high-spin LSDA state neglecting—in the case of more than a half-filled shell—the interaction with and within the majority spin subshell, which is canceled by the part $UMN+\frac{1}{2}(U-J)M(M-1)$ of the double-counting term. This means that the high-spin LSDA state is effectively treated as the LDA one (in the subspace of partially filled spin shell) with double-counting term described by the expression (12).

To shorten the derivations we rewrite expression (6) omitting the spin index in terms of $W_{mm'}=U_{mm'}-J_{mm'}$ and $W=U-J$

$$\sum_{m'} W_{mm'} = (M-1)W. \tag{22}$$

Summing also over $m$ one obtains

$$\sum_{mm'} W_{mm'} = M(M-1)W.$$

Expression (12) may now be rewritten as

$$\tilde{E} = \underline{N}\left[N - \frac{\underline{N}+1}{2}\right]W. \tag{23}$$

We find it convenient to use $\tilde{E}$ as the reference energy for both the interaction and double-counting term

$$E_{ee}^{*} = E_{ee} - \tilde{E}; \quad E_{\mathrm{dc}}^{*} = E_{\mathrm{dc}} - \tilde{E}.$$

Accordingly the values

$$\tilde{v}_0 = -\frac{\underline{N}(\underline{N}+1)}{2}W; \quad \tilde{v}_i = \underline{N}W$$

are subtracted from the corresponding potentials.

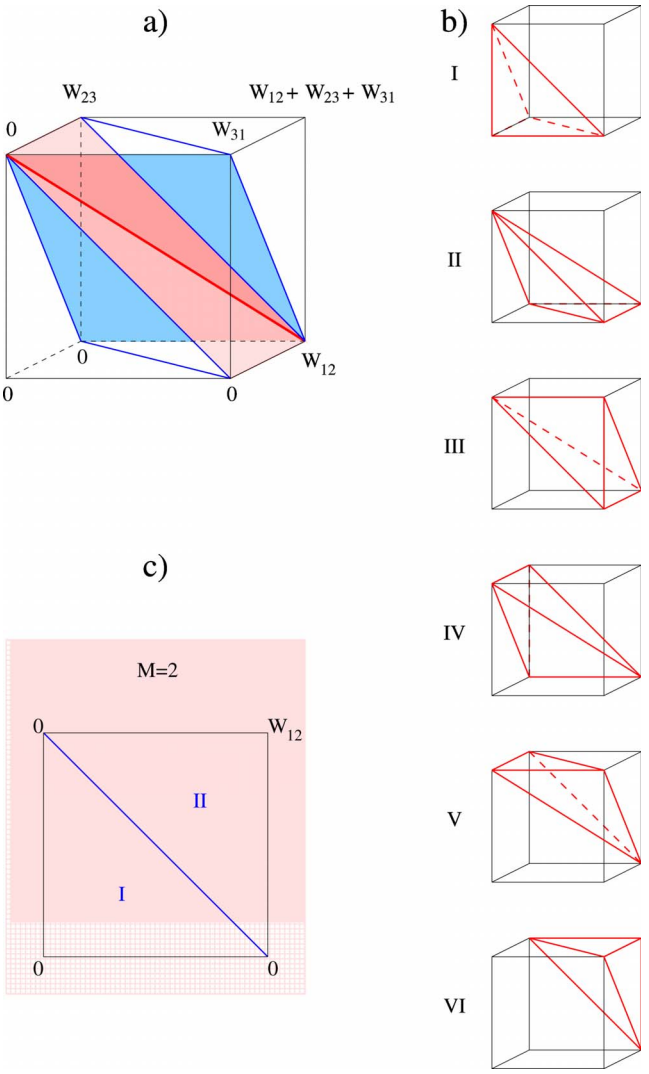


FIG. 1. (Color online) (a) The 19 leading diagonals (including 12 cube edges) and ten partitioning planes (including 6 cube faces) and (b) the six resulting simplices in the three-dimensional case. (c) The five leading diagonals (including 4 square edges) and two resulting simplices in the two-dimensional case. The partitioning "planes" coincide with the leading diagonals.

### A. $N \leq 1$ and $N \geq M-1$

These cases represent situations with less than one electron or one hole in the open shell, respectively. The first case is very simple. Both interaction and double-counting terms are identically zero. The solution for the hole case is

TABLE I. The weights $\omega_\mu$ for the four possible $\mu$ states in two simplex regions in the two-dimensional case.

| | I | II |
|---|---|---|
| ∘∘ | $1-n_1-n_2$ | 0 |
| •∘ | $n_1$ | $1-n_2$ |
| ∘• | $n_2$ | $1-n_1$ |
| •• | 0 | $n_1+n_2-1$ |

TABLE II. The weights $\omega_\mu$ for eight possible $\mu$ states in six simplex regions in the three-dimensional case.

| | I | II | III |
|---|---|---|---|
| ∘∘∘ | $1-n_1-n_2-n_3$ | 0 | 0 |
| •∘∘ | $n_1$ | $1-n_2-n_3$ | $1-n_2-n_3$ |
| ∘•∘ | $n_2$ | $1-n_1-n_3$ | 0 |
| ∘∘• | $n_3$ | $n_3$ | $1-n_1$ |
| ••∘ | 0 | $n_1+n_2+n_3-1$ | $n_2$ |
| •∘• | 0 | 0 | $n_1+n_3-1$ |
| ∘•• | 0 | 0 | 0 |
| ••• | 0 | 0 | 0 |

| | IV | V | VI |
|---|---|---|---|
| ∘∘∘ | 0 | 0 | 0 |
| •∘∘ | 0 | 0 | 0 |
| ∘•∘ | $1-n_1-n_3$ | 0 | 0 |
| ∘∘• | $1-n_2$ | $2-n_1-n_2-n_3$ | 0 |
| ••∘ | $n_1$ | $1-n_3$ | $1-n_3$ |
| •∘• | 0 | $n_1+n_3-1$ | $1-n_2$ |
| ∘•• | $n_2+n_3-1$ | $n_2+n_3-1$ | $1-n_1$ |
| ••• | 0 | 0 | $n_1+n_2+n_3-2$ |

$$
\begin{aligned}
2E_{ee} &= \sum_{ij} (n_i + n_j - 1) W_{ij} \\
&= \sum_i n_i \sum_j W_{ij} + \sum_j n_j \sum_i W_{ij} - \sum_{ij} W_{ij} \\
&= N(M-1)W + N(M-1)W - M(M-1)W \\
&= (2N-M)(M-1)W.
\end{aligned}
$$

One can easily check that the reference energy in Eq. (23) is reduced to the same value and that $E_{\mathrm{dc}}^{*}=0$ as the considered domain is a single (corner) simplex containing both the occupation point and its projection on the main diagonal.

Thus both in the "less than one electron" and the "less than one hole" cases the $+V$ correction is identically zero and the calculation reproduces the L(S)DA result. Particularly there is no correction in the case $M=2$ ($s$ shell) presented in Fig. 1 and the Table I.

### B. $M=3$

This case corresponds to a partially filled $p$ spin subshell. The full solution is presented in Fig. 1 and Table II where we assumed $0<W_{12}<W_{13}<W_{23}$. As known from the previous example only the case $1 \leq N \leq 2$ may be of interest. The resulting energy of electron-electron interaction is presented in the Table III.

Before subtraction of the double-counting term one has to realize that all matrix elements in a $p$ shell are, in fact, equal[15]

$$W_{12} = W_{13} = W_{23} = W = F^0 - \frac{1}{5}F^2,$$

which immediately follows also from the sum rule in Eq. (22). Taking this fact into account it appears that the energy

TABLE III. The energies $E_{ee}=\frac{1}{2}\Sigma_{ij}n_{ij}W_{ij}$ inside six simplices in the three-dimensional case. $n_{ij}=\Sigma_{\mu}^{\{ij\}\in\mu}\omega_{\mu}$.

| | $n_{12}$ | $n_{13}$ | $n_{23}$ |
|---|---|---|---|
| I | 0 | 0 | 0 |
| II | $n_1+n_2+n_3-1$ | 0 | 0 |
| III | $n_2$ | $n_1+n_3-1$ | 0 |
| IV | $n_1$ | 0 | $n_2+n_3-1$ |
| V | $1-n_3$ | $n_1+n_3-1$ | $n_2+n_3-1$ |
| VI | $n_1+n_2-1$ | $n_1+n_3-1$ | $n_2+n_3-1$ |

is equal $(N-1)W$ in the whole region $1\leq N\leq 2$ and is perfectly canceled by the double-counting term, so that $E_{ee}^{*}=E_{\mathrm{dc}}^{*}=0$. Thus there is no $+V$ correction for the high spin state of a $p$ shell.

Note that in the case $W_{12}=W_{13}=W_{23}$ the 3-cube has three equivalent leading body diagonals (lbd), which corresponds to three equivalent ways of choosing the two partitioning planes intersecting along one of these diagonals [shaded planes in Fig. 1(a)]. The final result does not, however, depend on a particular choice.

### C. $M=5$

This case corresponds to a partially filled $d$ spin subshell. The next table presents the values of the matrix elements in a $d$ shell (the orbitals are labeled by corresponding $l_z$ values, the notation "$\bar{A}$" is used for "$-A$")

| | $F^0$ | $F^2$ | $F^4$ |
|---|---|---|---|
| $W_{\bar{2}\bar{1}}=W_{\bar{2}0}=W_{02}=W_{12}$ | 1 | $-\frac{8}{49}$ | $-\frac{3}{147}$ |
| $W_{\bar{1}\bar{1}}$ | 1 | $-\frac{5}{49}$ | $-\frac{8}{147}$ |
| $W_{\bar{2}1}=W_{\bar{1}2}$ | 1 | $-\frac{2}{49}$ | $-\frac{13}{147}$ |
| $W_{\bar{1}0}=W_{01}$ | 1 | $\frac{1}{49}$ | $-\frac{18}{147}$ |
| $W_{\bar{2}\bar{2}}$ | 1 | $\frac{4}{49}$ | $-\frac{23}{147}$ |

so that one arrives at the following inequalities:

$$W_{\bar{2}\bar{1}}=W_{\bar{2}0}=W_{02}=W_{12}<W_{\bar{1}\bar{1}}<W_{\bar{2}1}=W_{\bar{1}2}<W_{\bar{1}0}=W_{01}<W_{\bar{2}\bar{2}}, \tag{24}$$

valid in the whole physically relevant domain $F^4/F^2\leq 1$.[16]

Due to the rather high degeneracy of the matrix elements many $d$-faces of the 5-cube have multiple leading body diagonals. To be precise the 5-face (the 5-cube itself) has four lbd's and 12 (of 40) 3-faces have two lbd's. To avoid the problem we "infinitesimally" decrease the energy value of one of the cube vertices belonging to such a $d$-face to singularize the corresponding leading diagonal. If after this some other faces still have multiple leading diagonals the procedure is repeated. As soon as the partition of the 5-cube is found the original values of the vertex energies are used to obtain the final result. A short MATHEMATICA program was used for the calculation.

Distinct from the three-dimensional case the edge criterion appears to be not sufficient for unambiguous partition.

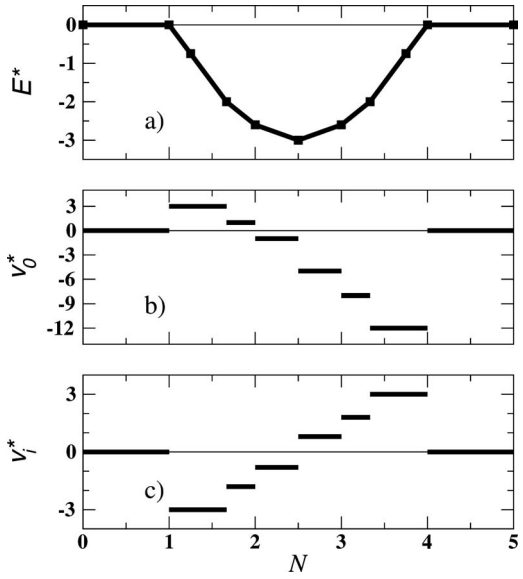


FIG. 2. The corrections (a) $E_{\mathrm{dc}}^{*}$, (b) $v_{\mathrm{dc};0}^{*}$, and (c) $v_{\mathrm{dc};i}^{*}$ in units of the modified Racah parameter $\tilde{B}$ for partially filled $d$ spin subshell $(M=5)$.

Apart from 120 correct minimizing simplices of equal volume 39 others were found and discarded using the procedure described at the end of Sec. V. The four partitioning planes $\Sigma_i n_i=N$ with $N=1,2,3,4$ separate the regions with different linear behavior of the reference energy in Eq. (23). The number of simplices contained in the cube "slabs" determined by the planes is 1, 26, 66, 26, and 1 in agreement with the general result on the volume of these slabs.[17]

After subtraction of the reference energy the isotropic part of the interaction $(F_0)$ cancels and all one-particle potentials $v_{ee}^{*}$ appear to be proportional to the Racah parameter $B=\frac{5}{49}(\frac{F^2}{5}-\frac{F^4}{9})$,[18] more precisely they are integer multiples of $\tilde{B}=\frac{3}{2}B$. The $+V$ energy correction $E_{ee}^{*}$ takes on the values from $-3\tilde{B}$ to $5\tilde{B}$ in the whole phase space of the orbital occupations $(n_{\bar{2}},n_{\bar{1}},n_0,n_1,n_2)$.

Also $E_{\mathrm{dc}}^{*}$ is not zero as in preceding examples. It is a piecewise linear function of $N/M$ having kinks at $\frac{1}{5},\frac{1}{3},\frac{2}{5},\frac{1}{2},\frac{3}{5},\frac{2}{3},\frac{4}{5}$. The function is shown in Fig. 2.

## VIII. CONCLUDING REMARKS

Our treatment of the double-counting term is based on the assumption that L(S)DA works perfectly for spherically symmetric atomic states. This assumption is, however, not justified. L(S)DA works much better for the states whose noninteracting counterpart reduces to a single determinant.[19] Therefore a more reasonable approach would be to define $E_{\mathrm{dc}}$ in such a way that it is equal to $E_{ee}$ at the vertices of the occupation cube and not at its main diagonal. However it would require an interpolation of the L(S)DA behavior into the domain of fractional orbital occupations. The behavior is certainly not linear contrary to that of the exact exchange-correlation functional.[20] In this sense the conventional AL double-counting term in Eqs. (10) and (11) may appear to be closer to reality than our assumption, as it interpolates the

TABLE IV. The orbital occupations of the high-spin eigenfunctions ($S_z=S$) for $M=5$ ($d$ spin subshell). $N$ is the number of electrons in the subshell. $\Psi$ is the multiplet ($LS$) state. $L_z$ is the projection of the orbital moment. The $d$ orbitals are labeled by $l_z$ values. The notation $\bar{A}$ is used for $-A$.

| $N$ | 0 | 1 | | | | | 2 | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\Psi$ | $^1S$ | $^2D$ | | | | | $^3P$ | | | $^3F$ | | | | | | |
| $L_z$ | 0 | $\bar{2}$ | $\bar{1}$ | 0 | 1 | 2 | $\bar{1}$ | 0 | 1 | $\bar{3}$ | $\bar{2}$ | $\bar{1}$ | 0 | 1 | 2 | 3 |
| $\bar{2}$ | 0 | 1 | 0 | 0 | 0 | 0 | $\frac{2}{5}$ | $\frac{4}{5}$ | 0 | 1 | 1 | $\frac{3}{5}$ | $\frac{1}{5}$ | 0 | 0 | 0 |
| $\bar{1}$ | 0 | 0 | 1 | 0 | 0 | 0 | $\frac{3}{5}$ | $\frac{1}{5}$ | $\frac{2}{5}$ | 1 | 0 | $\frac{2}{5}$ | $\frac{4}{5}$ | $\frac{3}{5}$ | 0 | 0 |
| 0 | 0 | 0 | 0 | 1 | 0 | 0 | $\frac{3}{5}$ | 0 | $\frac{3}{5}$ | 0 | 1 | $\frac{2}{5}$ | 0 | $\frac{2}{5}$ | 1 | 0 |
| 1 | 0 | 0 | 0 | 0 | 1 | 0 | $\frac{2}{5}$ | $\frac{1}{5}$ | $\frac{3}{5}$ | 0 | 0 | $\frac{3}{5}$ | $\frac{4}{5}$ | $\frac{2}{5}$ | 0 | 1 |
| 2 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | $\frac{4}{5}$ | $\frac{2}{5}$ | 0 | 0 | 0 | $\frac{1}{5}$ | $\frac{3}{5}$ | 1 | 1 |
| $N$ | 5 | 4 | | | | | 3 | | | | | | | | | |
| $\Psi$ | $^6S$ | $^5D$ | | | | | $^4P$ | | | $^4F$ | | | | | | |
| $L_z$ | 0 | 2 | 1 | 0 | $\bar{1}$ | $\bar{2}$ | 1 | 0 | $\bar{1}$ | 3 | 2 | 1 | 0 | $\bar{1}$ | $\bar{2}$ | $\bar{3}$ |
| $\bar{2}$ | 1 | 0 | 1 | 1 | 1 | 1 | $\frac{3}{5}$ | $\frac{1}{5}$ | 1 | 0 | 0 | $\frac{2}{5}$ | $\frac{4}{5}$ | 1 | 1 | 1 |
| $\bar{1}$ | 1 | 1 | 0 | 1 | 1 | 1 | $\frac{2}{5}$ | $\frac{4}{5}$ | $\frac{3}{5}$ | 0 | 1 | $\frac{3}{5}$ | $\frac{1}{5}$ | $\frac{2}{5}$ | 1 | 1 |
| 0 | 1 | 1 | 1 | 0 | 1 | 1 | $\frac{2}{5}$ | 1 | $\frac{2}{5}$ | 1 | 0 | $\frac{3}{5}$ | 1 | $\frac{3}{5}$ | 0 | 1 |
| 1 | 1 | 1 | 1 | 1 | 0 | 1 | $\frac{3}{5}$ | $\frac{4}{5}$ | $\frac{2}{5}$ | 1 | 1 | $\frac{2}{5}$ | $\frac{1}{5}$ | $\frac{3}{5}$ | 1 | 0 |
| 2 | 1 | 1 | 1 | 1 | 1 | 0 | 1 | $\frac{1}{5}$ | $\frac{3}{5}$ | 1 | 1 | 1 | $\frac{4}{5}$ | $\frac{2}{5}$ | 0 | 0 |

behavior of L(S)DA by a smooth parabolic dependence in the domain of the fractional total number of electrons in the open shell.

It is of course possible to use the conventional AL double-counting term also in combination with the interaction term in Eq. (16). It would restore the action of the isotropic part of the interaction absent in our approach due to the definition of the double-counting term in Eq. (21). For a noninteger number of electrons $N=\underline{N}+\bar{n}$ the conventional AL double-counting term adds an energy penalty[5]

$$\Delta E = \frac{\bar{n}(1-\bar{n})}{2} W,$$

which is the main effect promoting integer occupation of orbitals and represents mainly the correction of the L(S)DA self-interaction error.

For integer occupation numbers the variational interaction term coincides with the conventional one. The proposed method may, however, give a better description of the anisotropic interaction part for cases with fractional occupation of open-shell orbitals, which is an essential feature of the exact solution of the atomic problem. The anisotropic part promotes the orbital moments of the open-shell atom, driving it to Hund's state. It is remarkable that the $+V$ correction is zero for $s$ and $p$ elements (in LSDA high-spin state of the latter) corresponding to the experience that the "$+U$" correction is to be applied only to $d$ and $f$ elements.

Our method is suitable for the diagonal representation of the occupation matrix, which makes the diagonalization of the matrix unavoidable. This also means that the matrix elements have to be recalculated on the basis of natural open-shell orbitals. In general the elements should be different from those in standard spherical harmonic representation resulting in a different system of inequalities between the energies of determinantal states, which in turn may require a different partition of the occupation cube.

Finally we address one more point concerning the introduction of the variational interaction term in Sec. V. It may be argued that in the context of rotationally invariant L(S)DA+$U$ a correct definition of an ensemble state should involve not determinantal states but the eigenstates of the atomic problem solved in the subspace of a given open-shell configuration. In this case the functional Eq. (16) transforms into

$$E_{ee}(\boldsymbol{n}) = \inf_{\omega_{\mathfrak{m}}} \left\{ \sum_{\mathfrak{m}} \omega_{\mathfrak{m}} \mathcal{E}_{\mathfrak{m}} \middle| 0 \le \omega_{\mathfrak{m}}, \ \sum_{\mathfrak{m}} \omega_{\mathfrak{m}} = 1, \ \sum_{\mathfrak{m}} \omega_{\mathfrak{m}} \boldsymbol{n}_{\mathfrak{m}} = \boldsymbol{n} \right\}, \tag{25}$$

where $\mathfrak{m}$ is a set of quantum numbers characterizing the eigenstates $\Psi_{\mathfrak{m}}=\Sigma_\mu c_{\mu\mathfrak{m}}\Phi_\mu$ with energies $\mathcal{E}_{\mathfrak{m}}$. The components of orbital occupations $\boldsymbol{n}_{\mathfrak{m}}$ are computed as

$$n_{\mathfrak{m};i} = \sum_{\mu}^{\{i\}\in\mu} |c_{\mu\mathfrak{m}}|^2.$$

The minimization problem in Eq. (25) can be solved in the way described in Sec. V by replacing $\mu_i$ with $n_{\mathfrak{m};i}$ in construction of the columns of the matrix in Eq. (18). The

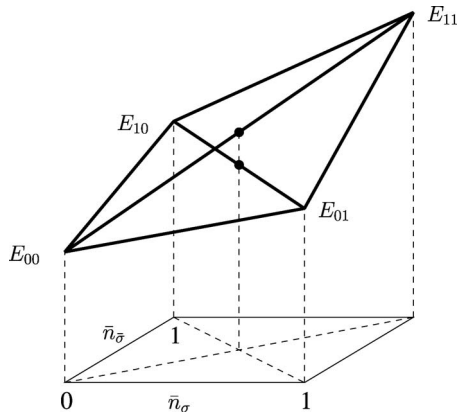


FIG. 3. The lifted point configuration for computation of the LSDA double-counting term.

points $\boldsymbol{n}_{\mathrm{m}}$ form vertices of a convex polytope lying inside the occupation cube and the solution is obtained by means of regular triangulation of the polytope as described in Sec. V. The columns of Table IV show the vertices of the corresponding polytope in the case of the $d$ spin subshell under the assumption that the angular part of the natural open-shell orbitals is represented by standard spherical harmonics.

An obvious disadvantage of the functional Eq. (25) is the fact that the corresponding polytope does not cover the whole occupation cube, so that the functional is undefined for occupation points lying outside the polytope. Further investigation of the functional is beyond the scope of this paper.

## ACKNOWLEDGMENTS

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## APPENDIX A: LSDA DOUBLE-COUNTING TERM

Let $N_\sigma=\underline{N}_\sigma+\bar{n}_\sigma$ and $N_{\bar{\sigma}}=\underline{N}_{\bar{\sigma}}+\bar{n}_{\bar{\sigma}}$. The point lies inside the square $0\leq\bar{n}_\sigma,\bar{n}_{\bar{\sigma}}\leq 1$ of the $(N_\sigma,N_{\bar{\sigma}})$ plane. At the vertices of the square the energies in Eq. (10) take the values

$$E_{i\bar{i}}=UN_iN_{\bar{i}}+\frac{1}{2}(U-J)[N_i(N_i-1)+N_{\bar{i}}(N_{\bar{i}}-1)],$$

where $N_i=\underline{N}_\sigma+i$, $N_{\bar{i}}=\underline{N}_{\bar{\sigma}}+\bar{i}$, $i(\bar{i})=0,1$. The energies are shown in Fig. 3 as vertices of a three-dimensional tetrahedron (the lifted point configuration discussed in Sec. V). Any convex combination of vertices represent a point inside the tetrahedron. The $(E_{01},E_{10})$ segment lies below the $(E_{00},E_{11})$ as can be easily checked for the corresponding energies of their midpoints

$$\frac{1}{2}(E_{00}+E_{11})-\frac{1}{2}(E_{01}+E_{10})=\frac{U}{2}.$$

Therefore the lowest possible energies are reached in the triangles $(E_{00},E_{01},E_{10})$ and $(E_{01},E_{10},E_{11})$ for $\bar{n}_\sigma+\bar{n}_{\bar{\sigma}}\leq 1$ and $\bar{n}_\sigma+\bar{n}_{\bar{\sigma}}\geq 1$, respectively. The corresponding weights can be found in Table I. After straightforward algebra one arrives at expression (13).

It is of some interest to note that if the values of the function $\pi(\bar{n}_\sigma,\bar{n}_{\bar{\sigma}})$ defined in Sec. IV are used as the corresponding weights one obtains for the double-counting term the expression

$$UN_\sigma N_{\bar{\sigma}}+\frac{1}{2}(U-J)\sum_\sigma[N_\sigma(N_\sigma-1)+\bar{n}_\sigma\underline{n}_\sigma].$$

## APPENDIX B: THE $\pi_\mu$ FUNCTION

We prove that

$$\sum_\mu \pi_\mu(\boldsymbol{x})=1 \tag{B1}$$

by induction. Assume that the equality is valid for binary vectors $\mu$ of dimension $N$ and consider the sum in Eq. (B1) for vectors of dimension $N+1$

$$\sum_\mu^{[\mu]=N+1}\pi_\mu(\boldsymbol{x})=[x_{N+1}+(1-x_{N+1})]\sum_\mu^{[\mu]=N}\pi_\mu(\boldsymbol{x})=1, \tag{B2}$$

where $[\mu]$ denotes the dimension of vector $\mu$. As the equality in Eq. (B1) is obvious for the binary vectors of dimension $N=1$ it is true for vectors of arbitrary dimension.

Let $\lambda_k$ be a binary vector of dimension $K$, $k$ being a subset of indices $[1,\ldots,N]$. Then

$$\sum_\mu^{\lambda_k\in\mu}\pi_\mu(\boldsymbol{x})=\pi_{\lambda_k}(\boldsymbol{x}_k),$$

where $\boldsymbol{x}_k$ is the corresponding subset of $\boldsymbol{x}$ and $\lambda_k\in\mu$ means (different from the definition given in Sec. IV) that $\mu_{k_i}=\lambda_{k_i}$ for all $k_i$. The proof is similar to Eq. (B2). Particularly, if $\lambda_k$ is a "1" vector

$$\sum_\mu^{\lambda_k\in\mu}\pi_\mu(\boldsymbol{x})=\prod_{i\in k}x_i\equiv\boldsymbol{x}_k^{\boldsymbol{\lambda}_k}.$$

## APPENDIX C: THE EDGE CRITERION

We precede the formulation and proof of the edge criterion by some definitions.

*Definitions.* A $d$-face of the $(0,1)^n$ cube is a $d$-dimensional cube, which is the convex hull of the $n$-cube vertices with $n-d$ coordinates fixed.

A body diagonal of a $(0,1)^n$ cube with dimension $n$ larger than zero is a segment connecting a pair of its opposite vertices $\mu$ and $\bar{\mu}$ $(\bar{\mu}_i=1-\mu_i)$. The sum $E_\mu+E_{\bar{\mu}}$ is assigned to the body diagonal. The diagonal with the smallest value of the sum is referred to as the leading body diagonal. A segment connecting a pair of the cube vertices is referred to as the leading diagonal of the cube if it is the leading body diagonal of a cube face.

An inscribed simplex is the convex hull of $n+1$ affinely independent cube vertices. The simplex delivers at any point the energy $\Sigma_\mu \omega_\mu E_\mu$, where $E_\mu$ are the energies assigned to the vertices and $\omega_\mu$ are the barycentric coordinates of the point with respect to the simplex.

A minimizing simplex is an inscribed simplex delivering at any point not larger energy than any other inscribed simplex.

A $n$-cube has $2^{n-d}\binom{n}{d}$ $d$ faces, each $d$-face with dimension larger than zero having $2^{d-1}$ body diagonals. The single—and therefore the leading—diagonal of a 1-cube (segment) is the 1-cube itself.

*Proposition.* Any edge of a minimizing simplex is a leading diagonal of the cube.

The proof can be sketched in the following way. Any edge of the simplex is a segment connecting two vertices of the cube. It is a body diagonal of some cube face determined by fixing the common coordinates of the vertices. Assume that the diagonal is not leading. The face has dimension $d>1$ and can contain up to $d+1$ vertices of the simplex. Note that no two vertices of the simplex can form another body diagonal of the face as the four vertices would lie in the same two-dimensional plane. This means that any simplex having the leading body diagonal of the cube face as an edge is different from the considered simplex and delivers a smaller energy value at the face center where the diagonals intersect each other in the middle point. This contradicts the assumption that the original simplex is minimizing and completes the proof.

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