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Ionization potentials from the extended Koopmans' theorem applied to density matrix functional theory

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Abstract

The Lagrangian matrix of the density matrix functional theory (DMFT) is shown to be identical with the generalized Fock matrix that enters the extended Koopmans' theorem (EKT), opening an avenue to computations of ionization potentials that avoids multiple energy-difference calculations. The performance of this new DMFT–EKT formalism is demonstrated with the 'primitive' DMFT functionals as an example.
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1. Introduction

The density-matrix functional theory (DMFT), in which the one-electron reduced density matrix (the 1-matrix) plays the role of the main quantity, provides yet another alternative to conventional electron correlation formalisms. Unlike the Kohn–Sham (KS) [1] implementation of the density functional theory, DMFT yields not only total energies and electron densities but also true natural orbitals, their occupation numbers, and (in some implementations) even the two-electron reduced density matrix (the 2-matrix) that can be employed in calculations of two-electron properties [2]. However, in contrast with the Hartree–Fock (HF) [3] and KS equations [4,5], where the resulting orbital energies approximate the ionization potentials (IPs), the eigenvalues that appear in the recently derived one-electron equations for the natural spinorbitals have no physical meaning (in fact they have no unique definition) [6].

The extended Koopmans' theorem (EKT) provides a connection between the 1- and 2-matrices of a Coulombic system and its ionization potentials [7–11]. In this Letter, we demonstrate how the combination of the DMFT formalism and EKT yields a practical method for computing IPs without resorting to multiple energy-difference calculations.

2. Theory

In density matrix functional theory (DMFT), the energy of the ground state is given by a functional of the one-electron reduced density matrix $\Gamma(\mathbf{x},\mathbf{x}')$ defined as

$$\Gamma(\mathbf{x},\mathbf{x}') = \sum_i n_i \varphi_i^*(\mathbf{x}')\varphi_i(\mathbf{x}), \qquad (1)$$

where $\mathbf{x}$ stands for the combined spatial and spin coordinates. The eigenvalues $\{n_i\}$ and eigenfunctions $\{\varphi_i(\mathbf{x})\}$ of the 1-matrix are called natural occupation numbers and natural spinorbitals, respectively. Assume that the total energy functional is written in terms of the natural occupancies and natural spinorbitals,

$$E[\Gamma] = E[\{n_i\}, \{\varphi_i\}] = \sum_i n_i h_{ii} + V_{ee}[\{n_i\}, \{\varphi_i\}], \qquad (2)$$

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where $V_{ee}[\{n_i\},\{\varphi_i\}]$ stands for the electron–electron interaction energy functional and $\{h_{ij}\}$ are the matrix elements of the core Hamiltonian

$$\hat{h}(\mathbf{x}) = -\frac{1}{2}\nabla_r^2 + v_{ext}(\mathbf{x}), \qquad (3)$$

with $v_{ext}(\mathbf{x})$ being the external potential.

In order to find the value of the functional corresponding to a ground state of the system under study, the r.h.s. of Eq. (2) should be minimized under the condition that the natural spinorbitals stay orthonormal whereas the natural occupation numbers conform to the N-representability conditions for Γ [12], i.e., they sum up to the number of electrons N and lie between 0 and 1. The orthonormality requirement and the normalization condition are easily taken into account by Lagrange multipliers. One is then led to the following functional

$$\Omega[\{n_i\},\{\varphi_i\}] = E[\{n_i\},\{\varphi_i\}] - \mu\left(\sum_i n_i - N\right)$$
$$- \sum_{ij}\lambda_{ij}\left(\langle\varphi_i|\varphi_j\rangle - \delta_{ij}\right), \qquad (4)$$

where the Lagrangian λ should be Hermitian. The functional (4) has to be stationary with respect to variations in $\{\varphi_i(\mathbf{x})\}$, $\{\varphi_i^*(\mathbf{x})\}$, and $\{n_i\}$, which in turn yields the following set of variational equations

$$\left(n_i\hat{h}(\mathbf{x}) + \frac{1}{\varphi_i(\mathbf{x})}\frac{\delta V_{ee}[\{n_j\},\{\varphi_j\}]}{\delta\varphi_i^*(\mathbf{x})}\right)\varphi_i(\mathbf{x}) = \sum_j \lambda_{ij}\varphi_j(\mathbf{x}) \qquad (5)$$

(an analogous set of equations results from taking a derivative with respect to $\{\varphi_i(\mathbf{x})\}$) and

$$h_{ii} + \frac{\partial V_{ee}[\{n_k\},\{\varphi_k\}]}{\partial n_i} = \mu. \qquad (6)$$

Consequently, the elements of the Lagrangian read

$$\lambda_{ij} = n_i h_{ji} + \int \frac{\delta V_{ee}[\Gamma]}{\delta\varphi_i^*(\mathbf{x})}\varphi_j^*(\mathbf{x})\,d\mathbf{x}. \qquad (7)$$

In order to show that λ is identical with the generalized Fock matrix that enters the extended Koopmans' theorem, one investigates the relation between the functional derivative of the electron–electron repulsion energy functional $V_{ee}[\Gamma] = V_{ee}[\{n_i\},\{\varphi_i\}]$ and the 2-matrix $\Gamma^{(2)}(\mathbf{x}_1',\mathbf{x}_2';\mathbf{x}_1,\mathbf{x}_2)$,

$$\Gamma^{(2)}(\mathbf{x}_1',\mathbf{x}_2';\mathbf{x}_1,\mathbf{x}_2) = \sum_{ijkl}\Gamma_{ijkl}^{(2)}\varphi_i^*(\mathbf{x}_1')\varphi_j^*(\mathbf{x}_2')\varphi_k(\mathbf{x}_1)\varphi_l(\mathbf{x}_2). \qquad (8)$$

The exact functional $V_{ee}[\Gamma]$ is defined through the constrained search [2]

$$V_{ee}[\Gamma] = \min_{\{\xi_p\}}\sum_{ijkl}\Gamma_{ijkl}^{(2)}(\{\xi_p\})\langle ij|kl\rangle, \qquad (9)$$

where

$$\langle ij|kl\rangle = \int\int \varphi_i^*(\mathbf{x}_1)\varphi_j^*(\mathbf{x}_2)|\mathbf{r}_1 - \mathbf{r}_2|^{-1}$$
$$\times \varphi_k(\mathbf{x}_1)\varphi_l(\mathbf{x}_2)\,d\mathbf{x}_1\,d\mathbf{x}_2 \qquad (10)$$

are the two-electron repulsion integrals over the natural orbitals and the parameterization with this set of parameters $\{\xi_p\}$ is such that

$$\forall_{\{\xi_p\}}\forall_{ij}\ 2(N-1)^{-1}\sum_k \Gamma_{ikjk}^{(2)}(\{\xi_p\}) = n_i\delta_{ij} \qquad (11)$$

and $\Gamma_{ijkl}^{(2)} \equiv \Gamma_{ijkl}^{(2)}(\{\xi_p\})$ is N-representable.

Thanks to the variational construction of the functional $V_{ee}[\Gamma]$, the first term in the r.h.s. of the equation

$$\frac{\delta V_{ee}[\Gamma]}{\delta\varphi_i^*(\mathbf{x})} = \sum_p \frac{\partial V_{ee}[\Gamma]}{\partial\xi_p}\frac{\delta\xi_p}{\delta\varphi_i^*(\mathbf{x})} + \sum_{jklm}\Gamma_{jklm}^{(2)}\frac{\delta\langle jk|lm\rangle}{\delta\varphi_i^*(\mathbf{x})} \qquad (12)$$

vanishes provided the gradient of $V_{ee}[\Gamma]$ with respect to $\{\xi_p\}$ exists. Consequently, one has

$$\int \frac{\delta V_{ee}[\Gamma]}{\delta\varphi_i^*(\mathbf{x})}\varphi_j^*(\mathbf{x})\,d\mathbf{x} = \int \sum_{klmn}\Gamma_{klmn}^{(2)}\frac{\delta\langle kl|mn\rangle}{\delta\varphi_i^*(\mathbf{x})}\varphi_j^*(\mathbf{x})\,d\mathbf{x}$$
$$= 2\sum_{klm}\Gamma_{iklm}^{(2)}\langle jk|lm\rangle. \qquad (13)$$

The equivalence of the Lagrangian λ with the generalized Fock matrix of EKT equations [7,8] is now evident, implying that diagonalization of the matrix Λ with the elements

$$\Lambda_{ij} = \frac{\lambda_{ij}}{\sqrt{n_i n_j}} \qquad (14)$$

yields ionization potentials as eigenvalues. Note that the matrix Λ is Hermitian for optimal 1-matrices (i.e., those for which the energy is stationary) that should be employed in actual calculation of ionization potentials. Interestingly, like in the case of the MCSCF approach, it may be shown that the antihermitian part of the Lagrangian [Eq. (7)] is equivalent to the gradient of the total energy with respect to elements of the unitary matrix that rotates the natural orbitals [13] and vanishes when the optimization procedure is completed. Alternatively, one observes that

$$\forall_{i\neq j}\ \lambda_{ij} - \lambda_{ji}^* = (n_i - n_j)\langle\varphi_j|h_{eff}|\varphi_i\rangle, \qquad (15)$$

where h_{eff} is a one-particle effective Hamiltonian introduced in [6] that is diagonal for the optimized natural orbitals.

For approximate electron–electron interaction functionals $V_{ee}[\Gamma]$, diagonalization of the matrix Λ will yield approximate ionization potentials. The accuracy of the

DMFT–EKT ionization potentials will hinge not only upon the quality of the functional $V_{ee}[\Gamma]$ itself but also on the quality of its functional derivatives with respect to the natural orbitals. In other words, accuracy of the approximation to the total energy does not guarantee that of the corresponding IPs. This point is well illustrated in the following section of this Letter.

It should be noted that the ionization potentials can be also obtained from the equation-of-motion approach [14]. Using the simple metric leads to the same working equations as in the EKT formalism, whereas the commutator metric results in the equations that involve only the 1-matrix elements (for a comparison see [15,16]). Although the latter approach seems suitable for the application to DMFT, it is not exact (unlike the EKT) even for two-electron systems with all occupation numbers different from zero, and will not be considered here.

3. The DMFT–EKT ionization potentials from the 'primitive' functionals

We applied the aforedescribed DMFT–EKT formalism to the so-called 'primitive' 1-matrix functionals [2,17–19], whose appealing feature is their simplicity. Unfortunately, it has been shown that the 'primitive' functionals (or more generally the 'JK-only' functionals) cannot be derived from the N-representable ansatz for the 2-matrix [20]. Although these functionals fail in the description of the homogeneous electron gas [21,22] and the simplest functionals of this class, namely the Buijse–Baerends (BB) functional [17,23], the Goedecker–Umrigar (GU) functional [18], and the corrected Hartree–Fock functional [24] are deficient in reproducing electron correlation in molecular systems [25–27], the recently proposed BBC3 (Buijse–Baerends-corrected) functional appears to offer a great improvement over its predecessors and produces very accurate energy curves for σ-bonded molecules [19]. Thus, their deficiencies notwithstanding, the 'primitive' functionals may remain a method of choice for DMFT calculations for a while.

All the 'primitive' 1-matrix functionals may be written in the following form

$$E[\Gamma] = \sum_i n_i h_{ii} + \frac{1}{2}\sum_{ij} n_i n_j \langle ij|ij\rangle + \frac{1}{2}\sum_{ij} F(n_i, n_j)\langle ij|ji\rangle,$$
(16)

where $F(x,y)$ is a function symmetrical with respect to the interchange of x and y. Here, we investigate the ionization potentials produced by the GU, BBC1, BBC2, and BBC3 functionals proposed for closed-shell systems, which are defined with (compare Eq. (16)):

$$F^{GU}(n_i, n_j) = \begin{cases} -n_i^2, & i = j, \\ -\sqrt{n_i n_j}, & \text{otherwise}, \end{cases}$$
(17)

$$F^{BBC1}(n_i, n_j) = \begin{cases} \sqrt{n_i n_j}, & i \neq j; i, j \in \text{virt}, \\ -\sqrt{n_i n_j}, & \text{otherwise}, \end{cases}$$
(18)

$$F^{BBC2}(n_i, n_j) = \begin{cases} \sqrt{n_i n_j}, & i \neq j; i, j \in \text{virt}, \\ -n_i n_j, & i \neq j; i, j \in \text{occ}, \\ -\sqrt{n_i n_j}, & \text{otherwise}, \end{cases}$$
(19)

$$F^{BBC3}(n_i, n_j) = \begin{cases} \sqrt{n_i n_j}, & i \neq j; i, j \in \text{virt}, \\ -n_i n_j, & i \neq j; (i, j \in \text{occ}) \\ & \vee (i \in \text{occ}, j \in \text{frn}) \\ & \vee (j \in \text{occ}, i \in \text{frn}), \\ -n_i^2, & i = j; i \notin \text{frn}, \\ -\sqrt{n_i n_j}, & \text{otherwise}. \end{cases}$$
(20)

In the case of the BBC3 functional the natural orbitals are divided into the groups of strongly occupied (occ), weakly occupied (virt), and frontier (frn) (note that an orbital may be of the 'virt' and 'frn' type at the same time), whereas for BBC1 and BBC2 the orbitals are considered to be either strongly or weakly occupied [19].

In our calculations, the natural spinorbitals and natural occupation numbers were obtained in a self-consistent manner with the algorithm described previously [19]. The DMFT–EKT ionization potentials were computed by diagonalizing the matrix Λ [Eq. (14)] the elements of which have a particularly simple form for the 'primitive' functionals, namely

$$\Lambda_{ij} = \sqrt{\frac{n_i}{n_j}}\left[h_{ji} + \sum_k n_k \langle jk|ik\rangle + \frac{1}{n_i}\sum_k F(n_i, n_k)\langle jk|ki\rangle \right].$$
(21)

Although it is not evident from its structure, the matrix Λ is Hermitian for the self-consistently obtained 1-matrix as it represents the elements of the Lagrangian divided by the square roots of the product of the occupation numbers (compare Eqs. (7) and (14)). The calculations were carried out for the He, Be, and Ne atoms and the LiH, Li_2, HF, and N_2 molecules. For the atoms, the cc-pVQZ [28] basis set was employed with the exclusion of the g and one of the f orbitals for Be and Ne. For the molecules, a smaller cc-pVTZ basis set was used from which f and one d orbitals were excluded for atoms in the Li_2 and N_2 molecules. Table 1 lists the total energies afforded by the functionals under study. In Table 2, the computed DMFT–EKT ionization potentials are compiled together with the Hartree–Fock orbital energies and the corresponding experimental values.

Inspection of the results confirms that the trends exhibited by the functionals in reproducing the IPs do not parallel those for the total energies. Except for the He atom, the relative errors in the correlation energies are the largest for the BBC1 functional (the average

Table 1
Comparison of the total energies (a.u.) and correlation energies errors (%) for the BBC1, BBC2, BBC3, and GU functionals[a]

Species	FCI[b]/MRSDCI	BBC1	BBC2	BBC3	GU
He	−2.90241	−2.90414 (4)	−2.90414 (4)	−2.89760 (−12)	−2.89784 (−11)
Be	−14.64005	−14.67845 (57)	−14.67412 (51)	−14.64231 (3)	−14.65777 (26)
Ne	−128.82734[c]	−128.88155 (19)	−128.86591 (14)	−128.83354 (2)	−128.85899 (11)
LiH	−8.03670	−8.05540 (37)	−8.05486 (36)	−8.04254 (12)	−8.04312 (13)
Li$_2$	−14.92918	−14.97231 (75)	−14.96810 (67)	−14.94192 (22)	−14.95730 (49)
HF	−100.33887[c]	−100.41018 (25)	−100.38434 (16)	−100.33413 (−2)	−100.36258 (8)
N$_2$	−109.29215[c]	−109.47022 (54)	−109.41370 (37)	−109.30666 (4)	−109.40721 (35)

[a] The correlation energy errors with respect to FCI or MRSDCI are given in parentheses. The following bond lengths were used: $R_{LiH} = 3.016$ (a.u.), $R_{Li_2} = 5.052$ (a.u.), $R_{HF} = 1.733$ (a.u.), $R_{N_2} = 2.072$ (a.u.).
[b] The full-CI calculations were carried out for the He, Be, LiH, and Li$_2$ species.
[c] Ref. [29].

Table 2
Comparison of ionization potentials (eV) and their relative errors (%)[a]

Species	NO	HF	BBC1	BBC2	BBC3	GU	Exp.
He	1s	24.98 (1.5)	24.37 (−0.9)	24.37 (−0.9)	25.98 (5.6)	24.52 (−0.3)	24.59[b]
Be	2s	8.42 (−9.8)	9.51 (1.9)	9.37 (0.4)	8.74 (−6.3)	8.28 (−11.3)	9.32[c]
	1s	128.78 (5.3)	118.83 (−2.8)	121.78 (−0.4)	124.36 (1.7)	127.46 (4.2)	122.29[c]
Ne	2p	23.10 (7.1)	22.11 (2.5)	22.59 (4.8)	22.02 (2.1)	21.69 (0.6)	21.56[d]
LiH	σ	8.20 (6.5)	7.84 (1.7)	7.86 (2.0)	7.50 (−2.6)	7.99 (3.7)	7.70[e]
Li$_2$	σ	4.94 (−3.8)	6.01 (17.0)	5.97 (16.1)	5.02 (−2.3)	4.84 (−5.8)	5.14[f]
HF	π	17.50 (8.1)	17.73 (9.5)	17.67 (9.1)	17.03 (5.2)	16.50 (1.9)	16.19[g]
	σ	20.69 (7.8)	19.28 (0.5)	20.30 (5.8)	19.64 (2.4)	20.01 (4.3)	19.19[g]
N$_2$	σ$_g$	17.28 (10.7)	18.51 (18.7)	17.12 (9.7)	16.44 (5.4)	15.96 (2.3)	15.60[g]
	π$_u$	16.75 (0.4)	17.45 (4.6)	17.74 (6.4)	17.27 (3.5)	16.67 (0.0)	16.68[g]
	σ$_u$	21.18 (12.8)	20.58 (9.6)	21.00 (11.8)	20.57 (9.5)	20.58 (9.6)	18.78[g]

[a] The relative errors of the ionization potentials with respect to the experimental values are given in parentheses. See footnote of Table 1 for the bond lengths used.
[b] Ref. [7].
[c] Ref. [9].
[d] Ref. [4].
[e] Ref. [30].
[f] Ref. [31].
[g] Ref. [32].

relative error (AE) amounting to 39%), smaller for the BBC2 (AE = 32%) and the GU (AE = 22%) functionals, and finally the smallest for the BBC3 functional (AE = 8%). On the other hand, the errors in the calculated ionization potentials are less systematic, the most striking example being the Be atom for which the BBC1 and BBC2 functionals that produce the least accurate total energies, yield the most accurate first IP. On average, however, the BBC3 and GU functionals perform better in reproducing the ionization potentials than BBC1 and BBC2 although their superiority is definitely less pronounced than in case of the total energies as the average relative errors in IPs obtained with the BBC1, BBC2, BBC3, and GU formulae amount to 6%, 6%, 4%, and 4%, respectively. Thus, the 1-matrix functionals under study in most cases provide only a very modest improvement in the IPs over the HF approach, for which the average relative error equals 7%. In case of the N$_2$ molecule, for which the HF ionization

potentials for the σ$_g$ and π$_u$ orbitals are in the wrong order comparing with the experimental values, only the BBC1 functional fails to restore the correct ordering.

4. Conclusions

Upon application of the constrained search formalism to the density matrix functional theory (DMFT), it turns out that the functional derivatives of the electron–electron repulsion energy functional with respect to the natural spinorbitals are related to the partial contraction of the 2-matrix with the two-electron integrals. The relation enables one to show that the variational DMFT equations for natural spinorbitals are equivalent to those of the extended Koopmans' theorem. Consequently, computation of ionization potentials within DMFT is now possible without multiple energy-difference calculations.

The new DMFT–EKT formalism has been applied to the 'primitive' DMFT functionals. The results obtained for a small set of atoms and diatomic molecules reveal that, on average, the accuracy of the approximate ionization potentials is not directly related to that of the corresponding total energy values. Thus the new formalism provides the means for independent assessment of approximate functionals of DMFT.

Acknowledgments

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