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Comparative metathermodynamic description of thermal and correlation electron effects

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Unified metathermodynamic description of thermal and correlation electron effects is proposed. It is based on the temperature-dependent populations of the common for all temperatures basis states of the (formally accurate) configuration interaction (CI) expansion of the components of the canonical ensemble. These populations are incorporated into the effective ensemble of the metathermodynamic approach through the partial effective temperatures. The extended temperature T_e is introduced as the statistical average of those temperatures. The absolute zero of the T_e scale represents a "no-correlation" Hartree-Fock state, while elevated T_e describes the increase of the "correlation motion" and the conventional thermal motion. The diagonal double configuration interaction (DDCI) approximation is considered, in which the proposed metathermodynamic description of thermal and correlation electron effects is based on the temperature-dependent orbital populations.

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I. INTRODUCTION

Despite their distinctive differences, thermal and electron correlation microscopic phenomena exhibit also common features, which suggest their comparison. From a formal qualitative point of view, both phenomena are caused by certain type of "motion". Behind thermal effects is a physical motion of particle constituents (molecules, atoms, and subatomic particles) of a system represented with the thermodynamic temperature T. In its turn, the Coulomb electron correlation can be depicted with the effective concerted "motion" of electrons in the configurational space to avoid each other and to reduce their mutual repulsion. The latter "motion" is represented with the correlation energy E_c.

The important unifying feature of thermal and electron correlation phenomena is that both are described in statistical quantum mechanics and in many-electron theory, respectively, with population of excited states in addition to the ground state. In the former theory these are the temperature-independent excited eigenstates $\Psi_{P>0}(0)$ of the Nth order density matrix (NDM) $\Gamma^N(T)$ [1,2]

$$\Gamma^N(T) = \sum_P w_P(T)|\Psi_P(0)\rangle\langle\Psi_P(0)|, \tag{1}$$

populated with the temperature-dependent weights $w_P(T)$. We consider a canonical ensemble, which is characterized with the free energy $F(T)$

$$F(T) = \sum_P w_P(T)E_P(0) + \sum_P T w_p(T)\ln(w_p(T)), \tag{2}$$

where the first sum is the energy term, while the second term is the entropy term.

In Eqs. (1) and (2) the ensemble weights $w_P(T)$ are determined with the Boltzmann formula

$$w_P(T) = \frac{\exp(-E_P(0)/T)}{Z(T)}, \tag{3}$$

where $Z(T)$ is the partition function

$$Z(T) = \sum_P \exp(-\frac{E_P(0)}{T}). \tag{4}$$

In Eqs. (3) and (4) $E_P(0)$ is the state energy

$$E_P(0) = \langle\Psi_P(0)|\hat{H}^N|\Psi_P(0)\rangle, \tag{5}$$

with $\hat{H}^N$ being the N-electron Hamiltonian.

On the other hand, at $T = 0$ the correlation effect in the ground and excited states $\Psi_P(0)$ is described with population within the configuration interaction (CI) of the single Φ_i^a, double Φ_{ij}^{ab}, and higher excitations of the reference determinant Φ_0 [3]

$$\Psi_P(0) = c_{0,P}\Phi_0 + \sum_{i=1}^{N}\sum_{a>N} c_{i,P}^a\Phi_i^a + \sum_{i,j=1}^{N}\sum_{a,b>N} c_{ij,P}^{ab}\Phi_{ij}^{ab} + \cdots \tag{6}$$

Here, the indices i, j run over the occupied orbitals, while a, b run over the virtual orbitals of Φ_0.

In this paper, a comparative metathermodynamic description of thermal and correlation electron effects is proposed based on the total temperature-dependent populations $w_{\{i\}}^{\{a\}}(T)$

$$w_{\{i\}}^{\{a\}}(T) = \sum_P w_P(T)|c_{\{i\},P}^{\{a\}}|^2 \tag{7}$$

of the excitations $\Phi_{\{i\}}^{\{a\}}$ in the CI expansions (6) of the states $\Psi_P(0)$ in the canonical ensemble (1). Based on this description, the extended temperature scale is introduced, in which both thermal and correlation electron effects are uniformly represented with the extended temperature T_e (see Secs. II and III).

The introduced comparative description is illustrated with a simple approximation to Eq. (1), in which the ensemble states Ψ_P^{DD} are obtained with the diagonal-double

CI (DDCI). Within the DDCI, only the DD excitations Φ_{ii}^{aa} of the reference Φ_0 are included in the CI expansion (6). In this approximation, a comparative description of thermal and correlation electron effects is based on the temperature-dependent occupations $n_a^i(T)$ of the virtual orbitals ϕ_a

$$n_a^i(T) = \sum_P w_P(T) n_a^{i,P} \tag{8}$$

stemming from the DD excitations from the occupied orbital ϕ_i (See Sec. IV).

II. METATHERMODYNAMIC DESCRIPTION OF THERMAL AND CORRELATION ELECTRON EFFECTS AT ELEVATED TEMPERATURES $T > 0$

As was already mentioned in the Introduction, the development in this paper is based on the CI expansion of the states $\Psi_P(0)$ in the canonical ensemble *N*DM (1)

$$\Psi_P(0) = c_{0,P}\Phi_0 + \sum_{\{i\},\{a\}} c_{\{i\},P}^{\{a\}} \Phi_{\{i\}}^{\{a\}}, \tag{9}$$

where Φ_0 is the Hartree-Fock (HF) reference determinant and $\Phi_{\{i\}}^{\{a\}}$ are its excitations. The string $\{i\}$ contains the indices of the occupied HF orbitals ϕ_i, from which the excited electrons are taken, while the string $\{a\}$ collects the indices of the virtual HF orbitals ϕ_a, to which the electrons are transferred. Note that, in principle, the expansion (9) gives an accurate representation of the states $\Psi_P(0)$ in the full CI (FCI) limit, in which all possible excitations $\Phi_{\{i\}}^{\{a\}}$ in a sufficiently large basis are included.

To provide a unified metathermodynamic description of thermal and correlation electron effects at the elevated temperature $T > 0$, we introduce the following effective *N*DM $\tilde{\Gamma}^N(T_e(T))$:

$$\tilde{\Gamma}^N(T_e(T)) = w_0(T_e(T))|\Phi_0\rangle\langle\Phi_0| + \sum_{\{i\},\{a\}} w_{\{i\}}^{\{a\}}(T_e(T))\big|\Phi_{\{i\}}^{\{a\}}\big\rangle\big\langle\Phi_{\{i\}}^{\{a\}}\big|. \tag{10}$$

In order to connect it to the true ensemble (1), the weights $w_0(T_e(T))$ and $w_{\{i\}}^{\{a\}}(T_e(T))$ of the HF reference Φ_0 and its excitations $\Phi_{\{i\}}^{\{a\}}$ are set with Eq. (7) as their total populations in the CI expansion (9) of the states $\Psi_P(0)$ in the real canonical ensemble (1). To this end, we introduce the effective partial temperatures $T_0(T)$ and $T_{\{i\}}^{\{a\}}(T)$ which are fitted, in order that the corresponding Boltzmann formulas would reproduce the total CI populations

$$w_0(T_e(T)) = \sum_P w_P(T)|c_{0,P}|^2 = \frac{\exp(-E_0/T_0(T))}{\tilde{Z}(T_e(T))} \tag{11}$$

and

$$w_{\{i\}}^{\{a\}}(T_e(T)) = \sum_P w_P(T)\big|c_{\{i\},P}^{\{a\}}\big|^2 = \frac{\exp\big(-E_{\{i\}}^{\{a\}}/T_{\{i\}}^{\{a\}}(T)\big)}{\tilde{Z}(T_e(T))}. \tag{12}$$

In Eqs. (11) and (12), E_0 and $E_{\{i\}}^{\{a\}}$ are the energies of the determinants Φ_0 and $\Phi_{\{i\}}^{\{a\}}$

$$E_0 = \langle\Phi_0|\hat{H}^N|\Phi_0\rangle \tag{13}$$

and

$$E_{\{i\}}^{\{a\}} = \big\langle\Phi_{\{i\}}^{\{a\}}\big|\hat{H}^N\big|\Phi_{\{i\}}^{\{a\}}\big\rangle, \tag{14}$$

while $\tilde{Z}(T_e(T))$ is the effective partition function

$$\tilde{Z}(T_e(T)) = \exp\left(-\frac{E_0}{T_0(T)}\right) + \sum_{\{i\},\{a\}} \exp\left(-\frac{E_{\{i\}}^{\{a\}}}{T_{\{i\}}^{\{a\}}(T)}\right). \tag{15}$$

With Eqs. (10)–(15), the free energy $\tilde{F}(T_e(T))$ of the introduced effective ensemble reads

$$\begin{aligned}\tilde{F}(T_e(T)) = {} & w_0(T_e(T))E_0 + \sum_{\{i\},\{a\}} w_{\{i\}}^{\{a\}}(T_e(T))E_{\{i\}}^{\{a\}} \\ & + T_0(T)w_0(T_e(T))\ln(w_0(T_e(T))) \\ & + \sum_{\{i\},\{a\}} T_{\{i\}}^{\{a\}}(T)w_{\{i\}}^{\{a\}}(T_e(T))\ln(w_{\{i\}}^{\{a\}}(T_e(T))).\end{aligned} \tag{16}$$

As follows from Eqs. (7), (10), and (12), at elevated temperatures $T > 0$ both thermal and correlation electron effects contribute to the population of the determinants $\Phi_{\{i\}}^{\{a\}}$. Specifically, the former effect determines the temperature-dependent factors $w_P(T)$ in the right-hand side of Eq. (7), while the latter effect determines the temperature-independent factors $|c_{\{i\},P}^{\{a\}}|^2$. To describe this combined effect in a metathermodynamic fashion, we introduce an extended temperature $T_e(T)$ as the statistical average over the effective temperatures $T_0(T)$ and $T_{\{i\}}^{\{a\}}$ in Eqs. (11) and (12)

$$T_e(T) = \frac{w_0(T_e(T))T_0(T) + \sum_{\{i\},\{a\}}^{w_{\{i\}}^{\{a\}} > w_t} w_{\{i\}}^{\{a\}}(T_e(T))T_{\{i\}}^{\{a\}}(T)}{w_0(T_e(T)) + \sum_{\{i\},\{a\}}^{w_{\{i\}}^{\{a\}} > w_t} w_{\{i\}}^{\{a\}}(T_e(T))}, \tag{17}$$

where w_t is a chosen threshold. Apparently, the extended temperature corresponding to the zero conventional temperature $T = 0$ is not zero $T_e(0) > 0$, since at this temperature the excited determinant populations are provided with electron correlation. The case $T = 0$ will be considered in the next section.

III. METATHERMODYNAMIC DESCRIPTION OF ELECTRON CORRELATION AT $T = 0$

At $T = 0$ the metathermodynamic approach of the previous section describes the "residual motion" of electrons. Furthermore, the fictitious thermodynamic "freezing" of this motion is considered with further reducing of the extended temperature T_e below $T_e(0)$. To this end, we introduce the "correlation freezing" parameter τ and we consider the following extension of the effective *N*DM (10):

$$\tilde{\Gamma}(T_e(\tau)) = w_0(T_e(\tau))|\Phi_0\rangle\langle\Phi_0| + \sum_{\{i\},\{a\}} w_{\{i\}}^{\{a\}}(T_e(\tau))\big|\Phi_{\{i\}}^{\{a\}}\big\rangle\big\langle\Phi_{\{i\}}^{\{a\}}\big|. \tag{18}$$

Its weights represent a gradual "freezing" of electron correlation with the parameter τ decreasing from 1 to 0 as follows:

$$w_0(T_e(\tau)) = \exp\left(-\frac{E_0}{\tau T_0(0)}\right)\Big/\tilde{Z}(T_e(\tau)), \tag{19}$$

and

$$w_{\{i\}}^{\{a\}}(T_e(\tau)) = \exp\left(-\frac{E_{\{i\}}^{\{a\}}}{\tau T_{\{i\}}^{\{a\}}(0)}\right)\Big/\tilde{Z}(T_e(\tau)), \tag{20}$$

where $\tilde{Z}(T_e(\tau))$ is the corresponding effective partition function

$$\tilde{Z}(T_e(\tau)) = \exp\left(-\frac{E_0}{\tau T_0(0)}\right) + \sum_{\{i\},\{a\}} \exp\left(-\frac{E_{\{i\}}^{\{a\}}}{\tau T_{\{i\}}^{\{a\}}(0)}\right). \tag{21}$$

The functions of the correlation freezing parameter τ are assembled into the effective free energy $\tilde{F}(T_e(\tau))$

$$\begin{aligned}\tilde{F}(T_e(\tau)) = {} & w_0(T_e(\tau))E_0 + \sum_{\{i\},\{a\}} w_{\{i\}}^{\{a\}}(T_e(\tau))E_{\{i\}}^{\{a\}} \\ & + \tau T_0(0) w_0(T_e(\tau)) \ln(w_0(T_e(\tau))) \\ & + \tau \sum_{\{i\},\{a\}} T_{\{i\}}^{\{a\}}(0) w_{\{i\}}^{\{a\}}(T_e(\tau)) \ln\big(w_{\{i\}}^{\{a\}}(T_e(\tau))\big).\end{aligned} \tag{22}$$

Finally, the extended temperature $T_e(\tau)$ representing the "residual correlation motion" at a particular τ is introduced as the statistical average of the effective temperatures of the previous section taken at $T = 0$ and multiplied by τ

$$T_e(\tau) = \tau \frac{w_0(T_e(\tau))T_0(0) + \sum_{\{i\},\{a\}}^{w_{\{i\}}^{\{a\}} > w_t} w_{\{i\}}^{\{a\}}(T_e(\tau))T_{\{i\}}^{\{a\}}(0)}{w_0(T_e(\tau)) + \sum_{\{i\},\{a\}}^{w_{\{i\}}^{\{a\}} > w_t} w_{\{i\}}^{\{a\}}(T_e(\tau))}. \tag{23}$$

With this construction, at $\tau = 1$ the metathermodynamic description of this section turns to that of the previous section at $T = 0$. This point represents the full freezing of the thermal motion and no freezing of the "correlation motion". Indeed, only the ground state $\Psi_0(0)$ of the true ensemble (1) survives at $T = 0$, so that the population of the excited determinants is caused exclusively by the electron correlation in $\Psi_0(0)$

$$\begin{aligned} w_0(T_e(T = 0)) \equiv w_0(T_e(\tau = 1)) &= |c_{0,0}|^2 \\ &= \exp\left(-\frac{E_0}{T_0(0)}\right)\Big/\tilde{Z}(T_e(T = 0)) \end{aligned} \tag{24}$$

and

$$\begin{aligned} w_{\{i\}}^{\{a\}}(T_e(T = 0)) \equiv w_{\{i\}}^{\{a\}}(T_e(\tau = 1)) &= |c_{\{i\},0}^{\{a\}}|^2 \\ &= \exp\left(-\frac{E_{\{i\}}^{\{a\}}}{T_{\{i\}}^{\{a\}}(0)}\right)\Big/\tilde{Z}(T_e(T = 0)). \end{aligned} \tag{25}$$

At another ending point $\tau = 0$ only the reference HF determinant Φ_0 survives in the effective ensemble (18) the ultimate freezing of the electron "correlation motion". Because of this, $\tau = 0$ can be called the "no-corrrelation" point.

The present metathermodynamic description of thermal and correlation electron effects is culminated in the extended temperature scale T_e

$$T_e = \begin{cases} T_e(T), & T > 0 \\ T_e(\tau), & T = 0 \end{cases}. \tag{26}$$

It encompasses both combined thermal and correlation effect at elevated temperatures $T > 0$ and the electron correlation effect at $T = 0$. The important physical characteristic of uniformity of the extended scale is provided with the introduced metathermodynamic description, according to which in both segments of Eq. (26) T_e represents the population of the same set of the determinants $\Phi_{\{i\}}^{\{a\}}$.

From the conceptual point of view it is interesting to note that in the extended scale (26) the point $T = 0$ would correspond to the different system-dependent extended temperatures

$$T_e(T = 0) > 0. \tag{27}$$

So, in this scale $T = 0$ looses its character of the absolute zero temperature. Instead, the new absolute zero of the extended scale

$$T_e(\tau = 0) = 0 \tag{28}$$

represents a fundamental characteristic of a many-electron system, namely, the "no-correlation" point.

IV. APPROXIMATE METATHERMODYNAMIC DESCRIPTION OF THERMAL AND CORRELATION EFFECTS BASED ON THE ORBITAL POPULATIONS

In this section a general metathermodynamic description of thermal and electron correlation effects of the previous sections is illustrated in the case of a simple approximate DDCI expansion of the states $\Phi_P(0)$ of the closed-shell canonical ensemble (1)

$$\Psi_P(0) \approx \Psi_P^{DD}(0) = c_{0,P}\Phi_0 + \sum_{i,a} c_{ii,P}^{aa}\Phi_{ii}^{aa}. \tag{29}$$

In this approximation, the partial occupation $n_a^{i,P}$ of the virtual HF orbital ϕ_a in the state $\Phi_p(0)$ is just the (multiplied by N) square of the modulus of the corresponding coefficient in the expansion (29)

$$n_a^{i,P} = N\left|c_{ii,P}^{aa}\right|^2, \tag{30}$$

so its temperature-dependent occupation $n_a^i(T)$ stemming from the DD excitations from the orbital ϕ_i is given with Eq. (8).

These orbital occupations feature in the approximate metathermodynamic description of thermal and correlation electron effects at elevated temperatures $T > 0$, in which the effective NDM (10) turns to

$$\begin{aligned}\tilde{\Gamma}^N(T_e(T)) = {} & (1 - \sum_{\{i\},\{a\}} \frac{n_a^i(T)}{N})|\Phi_0\rangle\langle\Phi_0| \\ & + \sum_{\{i\},\{a\}} \frac{n_a^i(T)}{N}\left|\Phi_{ii}^{a}\right\rangle\left\langle\Phi_{ii}^{aa}\right|.\end{aligned} \tag{31}$$

They determine the corresponding effective temperatures $T_0(T)$ and $T_i^a(T)$ through the Boltzmann formula

$$1 - \sum_{i,a} \frac{n_i^a(T)}{N} = \exp\left(-\frac{E_0}{T_0(T)}\right)\Big/\tilde{Z}(T_e(T)) \tag{32}$$

and

$$\frac{n_a^i(T)}{N} = \exp\left(-\frac{E_{ii}^{aa}}{T_i^a(T)}\right) \Big/ \tilde{Z}(T_e(T)), \tag{33}$$

where $\tilde{Z}(T_e(T))$ is the effective partition function

$$\tilde{Z}(T_e(T)) = \exp\left(-\frac{E_0}{T_0(T)}\right) + \sum_{i,a} \exp\left(-\frac{E_{ii}^{aa}}{T_i^a(T)}\right). \tag{34}$$

In their turn, the effective temperatures determine the effective free energy $\tilde{F}(T_e(T))$

$$\begin{aligned}\tilde{F}(T_e(T)) = &\left(1 - \sum_{i,a} \frac{n_a^i(T)}{N}\right) E_0 + \sum_{i,a} \frac{n_i^a(T)}{N} E_{ii}^{aa} \\ &+ T_0(T)\left(1 - \sum_{i,a} \frac{n_a^i(T)}{N}\right) \ln\left(1 - \sum_{i,a} \frac{n_a^i(T)}{N}\right) \\ &+ \sum_{i,a} T_i^a(T) \frac{n_a^i(T)}{N} \ln\left(\frac{n_a^i(T)}{N}\right)\end{aligned} \tag{35}$$

and the extended temperature T_e

$$T_e(T) = \frac{\left(1 - \sum_{i,a} \frac{n_a^i(T)}{N}\right) T_0(T) + \sum_{i,a}^{n_a^i(T) \geqslant n_t} \frac{n_a^i(T)}{N} T_i^a(T)}{1 - \sum_{i,a} \frac{n_a^i(T)}{N} + \sum_{i,a}^{n_a^i(T) \geqslant n_t} \frac{n_a^i(T)}{N}} \tag{36}$$

through the partial orbital occupations $n_a^i(T)$.

The extension of T_e below $T_e(0)$ is carried out with the effective NDM

$$\begin{aligned}\tilde{\Gamma}^N(T_e(\tau)) = &\, w_0(T_e(\tau)) |\Phi_0\rangle\langle\Phi(0)| \\ &+ \sum_{i,a} w_i^a(T_e(\tau)) \big|\Phi_{ii}^{aa}\big\rangle\big\langle\Phi_{ii}^{aa}\big|,\end{aligned} \tag{37}$$

where the weights $w_0(T_e(\tau))$ and $w_i^a(T_e(\tau))$ incorporate the "correlation freezing" parameter τ

$$w_0(T_e(\tau)) = \exp\left(-\frac{E_0}{\tau T_0(0)}\right) \Big/ \tilde{Z}(T_e(\tau)) \tag{38}$$

and

$$w_i^a(T_e(\tau)) = \exp\left(-\frac{E_{ii}^{aa}}{\tau T_i^a(0)}\right) \Big/ \tilde{Z}(T_e(\tau)), \tag{39}$$

where

$$\tilde{Z}(T_e(\tau)) = \exp\left(-\frac{E_0}{\tau T_0(0)}\right) + \sum_{i,a} \exp\left(-\frac{E_{ii}^{aa}}{\tau T_i^a(0)}\right). \tag{40}$$

The introduced τ-dependent metathermodynamic quantities are assembled into the effective free energy

$$\begin{aligned}\tilde{F}(T_e(\tau)) = &\, w_0(T_e(\tau)) E_0 + \sum_{i,a} w_i^a(T_e(\tau)) E_{ii}^{aa} \\ &+ \tau T_0(0) w_0(T_e(\tau)) \ln(w_0(T_e(\tau))) \\ &+ \tau \sum_{i,a} T_i^a(0) w_i^a(T_e(\tau)) \ln\big(w_i^a(T_e(\tau))\big).\end{aligned} \tag{41}$$

At the "full-correlation" point $\tau = 1$ the weights $w_i^a(T_e(\tau = 1))$ are equal to the corresponding partial orbital occupations at $T = 0$ divided by N

$$w_i^a(T_e(\tau = 1)) = \frac{n_a^i(0)}{N}, \tag{42}$$

At the "no-correlation" point $\tau = 0$ the effective ensemble (37) reduces to the HF determinant Φ_0. The corresponding extended temperature in the interval $0 \leqslant \tau \leqslant 1$ reads

$$T_e(\tau) = \tau \frac{w_0(T_e(\tau)) T_0(0) + \sum_{i,a}^{w_i^a > w_t} w_i^a(T_e(\tau)) T_i^a(0)}{w_0(T_e(\tau)) + \sum_{i,a}^{w_i^a > w_t} w_i^a(T_e(\tau))}. \tag{43}$$

With Eqs. (36) and (43), the extended temperature scale (26) uniformly describes the "switching-on" of electron correlation with $T_e(0 \leqslant \tau \leqslant 1)$ as well as the combined thermal and correlation effect at elevated temperatures $T_e(T > 0)$.

V. CONCLUSIONS

In this paper a comparative description of thermal and correlation electron effects is proposed based on the temperature-dependent populations of the common set of the basis N-electron states, the HF reference determinant, and its excitations. These states feature in the (formally accurate) CI expansion of the states of the canonical ensemble.

Within the present metathermodynamic description, the effective ensemble of the basis states is introduced. Its characteristic feature is the partial effective temperatures providing a connection to the real ensemble. They allow us to uniformly describe the combined thermal and correlation electron effect at elevated temperatures as well as the electron correlation at $T = 0$.

The extended temperature T_e is proposed as the statistical average of the partial effective temperatures. In the T_e scale, "no-thermal-motion" point $T = 0$ of the conventional temperature scale is replaced with the "no-correlation" point $T_e = 0$ as the absolute zero. Then, the increase of T_e from $T_e = 0$ to $T_e(T = 0)$ represents the metathermodynamic increase of the "electron correlation motion" between the no-correlation and full-correlation points. Further increase of T_e represents the combined effect of the correlation and conventional thermal motion.

The proposed metathermodynamic approach is illustrated with the DDCI approximation. In this case, the above-mentioned comparative description is based on the temperature-dependent orbital occupations. This approximation can serve as the basis of further approximate schemes with a metathermodynamic description of electron correlation at both zero and elevate temperatures. Such a development would parallel the analogous development within density matrix functional theory (DMFT)[4–23], reported in our recent work [24] as well as in the finite-temperature extension of DMFT [25,26].

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[1] J. von Neumann, *Mathematical Foundations of Quantum Mechanics* (Priceton University Press, Princeton, NJ, 1955).
[2] F. Reif, *Statistical and Thermal Physics* (McGraw-Hill, New York,1965).
[3] A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory* (Dover, New York, 1989).
[4] P. O. Löwdin and H. Shull, Phys. Rev. **101**, 1730 (1956).
[5] T. L. Gilbert, Phys. Rev. B **12**, 2111 (1975).
[6] A. M. K. Müller, Phys. Lett. A **105**, 446 (1984).
[7] M. Buijse and E. J. Baerends, Mol. Phys. **100**, 401 (2002).
[8] S. Goedecker and C. J. Umrigar, Phys. Rev. Lett. **81**, 866 (1998).
[9] G. Csányi and T. A. Arias, Phys. Rev. B **61**, 7348 (2000).
[10] J. M. Herbert and J. E. Harriman, J. Chem. Phys. **118**, 10835 (2003).
[11] C. Kollmar and B. A. Heß, J. Chem. Phys. **120**, 3158 (2004).
[12] J. Cioslowski and K. Pernal, J. Chem. Phys. **120**, 10364 (2004).
[13] O. V. Gritsenko, K. Pernal, and E. J. Baerends, J. Chem. Phys. **122**, 204102 (2005).
[14] M. Piris, Int. J. Quant. Chem. **106**, 1093 (2006).
[15] D. R. Rohr, K. Pernal, O. V. Gritsenko, and E. J. Baerends, J. Chem. Phys. **129**, 164105 (2008).
[16] M. A. L. Marques and N. N. Lathiotakis, Phys. Rev. A **77**, 032509 (2008).
[17] N. N. Lathiotakis, S. Sharma, J. K. Dewhurst, F. G. Eich, M. A. L. Marques, and E. K. U. Gross, Phys. Rev. A **79**, 040501(R) (2009).
[18] N. N. Lathiotakis, N. I. Gidopoulos, and N. Helbig, J. Chem. Phys. **132**, 084105 (2010).
[19] L. M. Mentel, R. van Meer, O. V. Gritsenko, and E. J. Baerends, J. Chem. Phys. **140**, 214105 (2014).
[20] K. Pernal, J. Chem. Theor. Comp. **10**, 4332 (2014).
[21] M. Piris, Phys. Rev. Lett. **119**, 063002 (2017).
[22] R. van Meer, O. V. Gritsenko, and E. J. Baerends, J. Chem. Phys. **148**, 104102 (2018).
[23] O. V. Gritsenko and K. Pernal, Phys. Rev. A **100**, 012509 (2019).
[24] R. van Meer and O. V. Gritsenko, Phys. Rev. A. **100**, 032335 (2019).
[25] T. Baldsiefen, A. Cangi, and E. K. U. Gross, Phys. Rev. A **92**, 052514 (2015).
[26] K. J. H. Giesbertz and M. Ruggenthaler, Phys. Rep. **806**, 1 (2019).