PHYSICAL REVIEW A **78**, 022510 (2008)

Rayleigh-Schrödinger many-body perturbation theory for density functionals: A unified treatment of one- and two-electron perturbations

János G. Ángyán

Équipe Modélisation Quantique et Cristallographique, LCM3B, Institut Jean Barriol, UMR 7036, Nancy-University, CNRS Boîte Postale 239, F-54506 Vandœuvre-lès-Nancy, France

(Received 19 December 2007; published 13 August 2008)

A time-independent many-body Rayleigh-Schrödinger perturbation theory is developed for total energy functionals, which depend simultaneously on a wave function and on the associated electron density. The most prominent example of such functionals is the Kohn-Sham energy functional, but similar situations occur as well in quantum chemical solvent effect theories. In contrast to previous density-functional perturbation theories, formulated in terms of one-electron orbitals, the present approach provides energy and eigenvector corrections for a many-electron wave function that satisfies a nonlinear effective Schrödinger equation. While the perturbed eigenvalues of order n depend on the eigenvector corrections up to the nth order, perturbational corrections of the total energy functional satisfy Wigner's $(2n+1)$ rule by virtue of nontrivial cancelations between eigenvalue and double count corrections up to order n. As a direct consequence of the nonlinearity of the effective Schrödinger equation, the wave-function corrections of any order are obtained by the solution of a self-consistent equation involving the second functional derivative of the density functional. Explicit total energy corrections are elaborated up to the fourth order. It is shown that the present approach reproduces standard results of the density-functional perturbation theory for static one-electron perturbations. Furthermore, two variants of the long-range Møller-Plesset correlation energy corrections in the range-separated hybrid density-functional framework are derived and discussed.

DOI: 10.1103/PhysRevA.78.022510 PACS number(s): 31.15.E−, 31.15.xp, 71.15.Mb

I. INTRODUCTION

In the past 20 years, density-functional perturbation theory (DFPT) became a powerful tool to determine first- and higher-order response properties in molecules and solids [1,2]. DFPT was formulated first by Baroni [3] using a Green's-function (resolvent) technique for linear-response properties. In the context of the efficient calculation of higher-order response quantities, the importance of Wigner's $(2n+1)$ rule was pointed out [4] and further elaborated on by Gonze [5,6]. Gonze's variation-perturbation framework [7,8] has been generalized for nonorthogonal Kohn-Sham orbitals [9] as well. A common feature of these methods is that they are formulated in a one-electron (orbital) framework. This is understandable in the context of the Kohn-Sham theory, which is an effective independent-particle method, where many-body effects are taken into account via a density-dependent effective potential, obtained as the functional derivative of a nonlinear density functional. Since the perturbing external potential (e.g., nuclear displacement, external electromagnetic field, etc.) modifies the one-electron potential in the Kohn-Sham Hamiltonian, which is nonlinear in the electron density, a self-consistent procedure is necessary to obtain the perturbed orbitals and energies, in close analogy to the perturbed coupled Hartee-Fock perturbation equations.

One can envisage other situations in which the one-electron, independent-particle model cannot be maintained. For instance, in the recently proposed generalization of the Kohn-Sham method [10,11], which consists in replacing the noninteracting Kohn-Sham reference system by a weakly (long-range) interacting one, but retains an effective one-electron density-functional description of the short-range electron interactions via a density-dependent effective potential, the model Hamiltonian becomes nonlinear, while at the same time it has a many-body character. In this context, we have recently raised the question of whether it is possible to elaborate a general, time-independent Rayleigh-Schrödinger perturbation theory (RSPT) [12,13] for N-electron wave functions that satisfy a *nonlinear* many-body Hamiltonian [14]. In a study of long-range correlation corrections approximating London dispersion forces in the range-separated hybrid density-functional approach [14,15], the necessary second-order correlation corrections were derived. Nevertheless, the question of elaborating on a general perturbation theory for nonlinear Hamiltonians has been left open.

It should be noted that other types of model Hamiltonians, depending explicitly on the electron density, may lead to analogous perturbation theory problems. One can mention the case of quantum chemical solvent effect theories [16–18] based on some of the variants of the reaction field model [19]. Here the solvent potential depends on the charge density of the quantum chemically treated solute molecule. A reformulation of the RSPT for a solvent potential as perturbation has been discussed in Refs. [20,21], while the case of linear (density-independent) perturbations to a system described by a nonlinear reaction field Hamiltonian has been derived in Ref. [22]. According to our knowledge, specific problems of the perturbation theory related to the nonlinearity of density-dependent effective Schrödinger equations were first discussed by Tapia and his co-workers [23,24].

In all of the above-mentioned cases, the main difficulty in the development of a perturbation theory is related to the *nonlinear* character of the effective Schrödinger equation. This nonlinearity comes from a density-dependent term of the effective Hamiltonian, related either to the exchange-correlation density functional or to the density-dependent effective solvent (polarization) potential. A central result, which has been proven independently in the case of the DFPT [4–6] and in that of the nonlinear RSPT for solvent effect models [22], is that due to a nontrivial cancelation of terms at a given order, Wigner's $(2n+1)$ rule of perturbation theory [25–28] is satisfied for the derivatives of the total energy. The benefits of the $(2n+1)$ rule could be exploited, e.g., to calculate higher polarizabilities [8,29], and they also lead to significant simplifications in the second-order correlation energy corrections to effective solvent effect Hamiltonians [30] as well as in the range-separated hybrid (RSH) density-functional framework [14].

Various self-consistent-field (SCF) [31] and density-matrix [32] perturbation theories are also based on a nonlinear effective Hamiltonian, the Fockian. In this latter case, the nonlinearity is due to the Hartree-Fock potential, which depends on the first-order density matrix, instead of the density itself. Although this case will not be treated here, the generalization of the forthcoming results, by replacing the density as the central variable with the first-order density matrix, seems to be relatively straightforward [33].

Other type of perturbation theories specifically designed for the treatment of the electron correlation problem have been elaborated on in the past, based on a Kohn-Sham zeroth-order Hamiltonian. The prototype of such approaches is the Görling-Levy perturbation theory [34–36], (GLPT), which has been generalized in view of obtaining an explicit expression for the correlation potential [37–48]. Although the perturbed Hamiltonian of the GLPT has a similar nonlinear character as in the problems outlined above [36], the explicit treatment of nonlinearity could be avoided by performing the perturbation expansion of the correlation energy at constant density. However, as far as the initial density is not the exact Kohn-Sham density, the GLPT is supposed to be used iteratively by improving the correlation potential obtained as the functional derivative of the correlation energy correction obtained in the previous step. This is an implicit way to take into account the inherently nonlinear character of the problem.

It seems to be a challenging question whether it is possible to develop a general perturbation theory framework for nonlinear effective Schrödinger equations, which is equally valid for both one- and two-electron perturbations and handles the nonlinearity explicitly at each order. As mentioned previously, the family of approaches, which is often called density-functional perturbation theory in a narrower sense, was originally developed to treat one-particle perturbations [1]. Its formulation remains in the independent-particle framework, which makes it less obvious to generalize it for cases in which the perturbation is of two-particle nature, as in the explicit perturbational treatment of the electron correlation problem of the nonlinear case. In the following, it will be shown that such a common framework can be established for both kinds of perturbations. Starting from the condition that the total energy can be written as a minimum principle, applied to the normalized expectation value $\langle\Psi|\hat{H}|\Psi\rangle$ of a linear Hamiltonian, $\hat{H}$, plus a functional, $F[n]$, of the electron density, $n(\boldsymbol{r})=\langle\Psi|\hat{n}(\boldsymbol{r})|\Psi\rangle$, a general perturbation theory will be developed without specifying from the outset the nature of the perturbation itself. As illustrated by the examples given in Sec. IV, specific equations describing both one- and two-electron perturbations can be easily obtained from the general perturbation equations.

The main results of this paper consist in the elaboration of RSPT energy corrections for the total energy of model problems that can be described by nonlinear time-independent many-body Schrödinger equations. In addition to the general-order expressions, explicit second-, third- and fourth-order RSPT energy corrections are given in Eqs. (66), (68), and (77), respectively. Self-consistent equations to obtain first- and second-order wave-function corrections are derived as well in Eqs. (47) and (51). Higher-order generalization of the second-order perturbation expressions used in the range-separated hybrid+second-order Møller-Plesset (RSH+MP2) approach [14,15] is provided by Eqs. (106) and (109), and the second-order working equations (118) and (120) are derived for the case in which the conventional approximate Kohn-Sham determinant is considered as the zeroth-order approximation of the range-separated problem.

Section II is devoted to a presentation of the basic definitions for the RSPT for a nonlinear Schrödinger equation. Perturbational expansion is given for the functional and for the corresponding effective potential. The derivation of the perturbation expansion of the variational total energy expression and of the associated wave-function corrections is given and discussed in Sec. III. Section IV provides a few examples of application of the general theory, namely the coupled perturbed Kohn-Sham equations and the second-order Møller-Plesset long-range correlation energy corrections in the range-separated hybrid framework. Finally, conclusions and some perspectives will be presented in Sec. V.

II. RSPT FOR NONLINEAR SCHRÖDINGER EQUATIONS

A. General definitions

A wide class of model problems that provide a simplified representation of a fully interacting physical system can be defined by a variational total energy expression that includes a functional of the electron density,

$$E = \min_{\Psi\to N}\{\langle\Psi|\hat{H}|\Psi\rangle + F[n_\Psi]\}, \tag{1}$$

and leads to the associated *nonlinear* Euler-Lagrange (effective Schrödinger) equation,

$$\{\hat{H} + \hat{\Omega}[n_\Psi]\}|\Psi\rangle = \mathcal{E}|\Psi\rangle, \tag{2}$$

where $\hat{H}$ is an N-electron, possibly interacting Hamiltonian (not equal to the physical Hamiltonian), $F[n_\Psi]$ is a functional of the total electron density, $n_\Psi(\boldsymbol{r})=\langle\Psi|\hat{n}(\boldsymbol{r})|\Psi\rangle$, obtained from the normalized wave function as the expectation value of the electron density operator, $\hat{n}(\boldsymbol{r})=\sum_i^N\delta(\boldsymbol{r}-\boldsymbol{r}_i)$. A typical example of a model that leads to such a problem is the Kohn-Sham method. The Hamiltonian $\hat{H}$, appearing in Eq. (1), is $\hat{H}=\hat{T}+\hat{V}_{ne}$, where $\hat{T}$ is the kinetic energy operator and $\hat{V}_{ne}$ is the operator of the electron-nuclear attraction. The functional

$F[n_\Psi]$, associated with this particular model is $E_{\mathrm{Hxc}}[n_\Psi]$, the Hartree-exchange-correlation functional,

$$E_{\mathrm{Hxc}}[n] = F_{\mathrm{HK}}[n] - T_s[n], \tag{3}$$

i.e., the difference between the universal Hohenberg-Kohn functional [49]

$$F_{\mathrm{HK}}[n] = \min_{\Psi\to n}\langle\Psi|\hat{T}+\hat{W}_{ee}|\Psi\rangle \tag{4}$$

and the noninteracting kinetic energy functional, $T_s[n]$,

$$T_s[n] = \min_{\Psi\to n}\langle\Psi|\hat{T}|\Psi\rangle = \langle\Phi^{\mathrm{KS}}|\hat{T}|\Phi^{\mathrm{KS}}\rangle. \tag{5}$$

The effective Hamiltonian of the corresponding Euler-Lagrange equation, Eq. (2), is the noninteracting Kohn-Sham Hamiltonian, $\hat{T}+\hat{V}_{ne}+\hat{V}_{\mathrm{Hxc}}=\hat{T}+\hat{V}_s$, where $\hat{V}_s$ is the Kohn-Sham potential.

As another example of a quite different nature, one could cite the case of the reaction field solvent effect models [16–18]. Here the Hamiltonian $\hat{H}$ is the usual molecular Hamiltonian of the solute, while the functional $F[n]$ describes the electrostatic solvation energy as a quadratic functional of the solute multipole moments. Further specific examples, related to range-separated hybrid density-functional theory, will be discussed in Sec. IV.

The variation in Eq. (1) is performed for normalized N-electron wave functions, Ψ. The eigenvalue of the effective Schrödinger equation, $\mathcal{E}$, is the Lagrange multiplier, related to the normalization constraint on the wave function. The density-dependent potential operator, $\hat{\Omega}=\int d\boldsymbol{r}\,\omega(\boldsymbol{r})\hat{n}(\boldsymbol{r})$, is defined through the local scalar potential $\omega(\boldsymbol{r})$, functional derivative of $F[n_\Psi]$,

$$\omega(\boldsymbol{r})[n] = \frac{\delta F[n]}{\delta n(\boldsymbol{r})}. \tag{6}$$

As a consequence of the presence of a density-dependent (nonlinear) potential operator, $\hat{\Omega}[n_\Psi]$, the effective Hamiltonian of Eq. (2) itself is nonlinear, i.e., it depends on its own lowest eigenfunction. In contrast to the usual linear case, the eigenvalue $\mathcal{E}$ is *not* equal to the variational total energy. This latter can be obtained from the relationship between the eigenvalue, the expectation value of the potential operator, and the density functional, such as

$$E = \mathcal{E} - \langle\Psi|\hat{\Omega}|\Psi\rangle + F[n_\Psi] = \mathcal{E} - \int d\boldsymbol{r}\frac{\delta F[n]}{\delta n(\boldsymbol{r})}n(\boldsymbol{r}) + F[n_\Psi]. \tag{7}$$

The quantity $F[n_\Psi]-\langle\Psi|\hat{\Omega}|\Psi\rangle$ is usually called double count correction [50]. The term "double count" may be related to the fact that in the case of a second-order nonlinearity (e.g., Hartree-energy), the corresponding functional is half of the expectation value of the potential $2F[n_\Psi]=\langle\Psi|\hat{\Omega}|\Psi\rangle$. Although for general functionals (e.g., in DFT) the relationship can be more complicated, the DFT literature has retained this terminology in a wider sense. Since one is working on a model that is designed to reproduce the total energy and certain properties (e.g., electron density) of the physical system, it is plausible that the eigenfunctions and the corresponding eigenvalues of the auxiliary effective Schrödinger equation are not necessarily the same as those of the physical Hamiltonian.

Considering a partition of the Hamiltonian to a zeroth-order part and a perturbation, as $\hat{H}=\hat{H}^{(0)}+\lambda\hat{W}$, where λ is an order parameter to be set to 1 at the end of the procedure, the total energy $E(\lambda)$ can be developed in power series of λ. The perturbation $\hat{W}$ is a Hermitian one-or two-electron operator, whose nature will be specified later, in the context of the various applications of the general perturbation scheme, in Sec. IV. All three components, namely the eigenvalue of the effective Schrödinger equation, $\mathcal{E}$, the density functional, $F[n]$, and the expectation value of the potential operator, $\hat{\Omega}[n]$, are to be expanded in power series of λ. The total energy correction of a given order is given by the sum of three contributions, provided by the respective corrections of the same order.

B. Expansion of the charge density

The expectation value of the charge density operator

$$n_{\boldsymbol{r}}(\lambda) = \frac{\sum_{\mu=0}^{\infty}\sum_{\nu=0}^{\infty}\lambda^{\mu+\nu}\langle\Psi^{(\mu)}|\hat{n}_{\boldsymbol{r}}|\Psi^{(\nu)}\rangle}{\sum_{\mu=0}^{\infty}\sum_{\nu=0}^{\infty}\lambda^{\mu+\nu}\langle\Psi^{(\mu)}|\Psi^{(\nu)}\rangle} \tag{8}$$

can be expanded into Taylor series with respect to λ leading to

$$n_{\boldsymbol{r}}(\lambda) = \langle\Psi^{(0)}|\hat{n}_{\boldsymbol{r}}|\Psi^{(0)}\rangle + \sum_{m=1}^{\infty}\lambda^m n_{\boldsymbol{r}}^{(m)}. \tag{9}$$

In this work, the intermediate (correlation) normalization, $\langle\Psi^{(0)}|\Psi^{(0)}\rangle=1$ and $\langle\Psi^{(k)}|\Psi^{(0)}\rangle=0$ for $\forall k\neq 0$, will be adopted. The lowest-order density corrections can be written explicitly as

$$n_{\boldsymbol{r}}^{(1)} = \langle\Psi^{(0)}|\hat{n}_{\boldsymbol{r}}|\Psi^{(1)}\rangle + \langle\Psi^{(1)}|\hat{n}_{\boldsymbol{r}}|\Psi^{(0)}\rangle \tag{10}$$

and

$$n_{\boldsymbol{r}}^{(2)} = \langle\Psi^{(0)}|\hat{n}_{\boldsymbol{r}}|\Psi^{(2)}\rangle + \langle\Psi^{(2)}|\hat{n}_{\boldsymbol{r}}|\Psi^{(0)}\rangle\langle\Psi^{(1)}|\hat{n}_{\boldsymbol{r}} - \langle\hat{n}_{\boldsymbol{r}}\rangle|\Psi^{(1)}\rangle. \tag{11}$$

Note that this definition of $n_{\boldsymbol{r}}^{(2)}$ contains an explicit contribution, $-\langle\hat{n}_{\boldsymbol{r}}\rangle\langle\Psi^{(1)}|\Psi^{(1)}\rangle$, due to the intermediate normalization of the wave function. This is a difference with respect of the definition for the second-order charge density by Gonze [6], who used another normalization convention [28], leading to somewhat different explicit energy corrections at higher than third order.

The general definition of the mth-order charge density correction is given formally as

$$n_{\boldsymbol{r}}^{(m)} = \frac{1}{m!}\frac{d^m}{d\lambda^m}n_{\boldsymbol{r}}(\lambda)|_{\lambda=0}, \tag{12}$$

which leads to the charge density correction at arbitrary order,

$$n_{\boldsymbol{r}}^{(m)} = \langle \Psi^{(0)} | \hat{n}_{\boldsymbol{r}} | \Psi^{(m)} \rangle + \langle \Psi^{(m)} | \hat{n}_{\boldsymbol{r}} | \Psi^{(0)} \rangle + n_{\boldsymbol{r}}^{(\bar{m})}, \qquad (13)$$

where $n_{\boldsymbol{r}}^{(\bar{m})}$ collects all contributions coming from wave-function corrections of order lower than m, obeying the recursion formula,

$$n_{\boldsymbol{r}}^{(\bar{m})} = \sum_{j=1}^{m-1} \left\{ \langle \Psi^{(j)} | \hat{n}_{\boldsymbol{r}} - n_{\boldsymbol{r}}^{(0)} | \Psi^{(m-j)} \rangle - n_{\boldsymbol{r}}^{(m-j)} \sum_{i=1}^{j-1} \langle \Psi^{(i)} | \Psi^{(j-i)} \rangle \right\}. \qquad (14)$$

C. Expansion of the double count correction

Suppose that the density functional $F[n]$ can be expanded in Taylor series around $F[n^{(0)}]$, where $n^{(0)}(\boldsymbol{r}) = \langle \Psi^{(0)} | \hat{n}(\boldsymbol{r}) | \Psi^{(0)} \rangle$ is the density associated with the zeroth-order wave function. In terms of the density shift, $\Delta n_{\boldsymbol{r}} = n_{\boldsymbol{r}} - n_{\boldsymbol{r}}^{(0)}$, one has the following general expression:

$$F[n(\lambda)] = F[n^{(0)}] + \sum_{k=1}^{\infty} \frac{1}{k!} K^{(k)}_{\boldsymbol{r}_1,\ldots,\boldsymbol{r}_k} \prod_{p=1}^{k} \Delta n_{\boldsymbol{r}_p}(\lambda). \qquad (15)$$

Expanding the density shift itself in power series of the perturbation parameter, λ, as

$$\Delta n_{\boldsymbol{r}}(\lambda) = \sum_{m=1}^{\infty} \lambda^m n_{\boldsymbol{r}}^{(m)}(\lambda), \qquad (16)$$

the coefficient $F^{(k)}$ corresponding to the kth-order contribution to the power series,

$$F[n] - F[n^{(0)}] = \sum_{k=1}^{\infty} \lambda^k F^{(k)}, \qquad (17)$$

is given formally as

$$F^{(k)} = \frac{1}{k!} \left. \frac{d^k}{d\lambda^k} F[n(\lambda)] \right|_{\lambda=0}. \qquad (18)$$

In particular, the kth-order contribution can be written as

$$F^{(k)} = \sum_{m=1}^{k} \frac{1}{m!} K^{(m)}_{\boldsymbol{r}_1,\ldots,\boldsymbol{r}_m} \sum_{j_1=1}^{k-1} \cdots \sum_{j_m=1}^{k-1} \prod_{p=1}^{m} n_{\boldsymbol{r}_p}^{(j_p)} \delta\left(k - \sum_{p=1}^{m} j_p \right). \qquad (19)$$

For the sake of notational brevity, the functions $K^{(m)}_{\boldsymbol{r}_1,\ldots,\boldsymbol{r}_m}$, etc. have been defined as functional derivatives of $F[n]$, for instance

$$K^{(2)}_{\boldsymbol{r}\boldsymbol{r}'} = \frac{\delta^2 F}{\delta n(\boldsymbol{r}) \delta n(\boldsymbol{r}')} = \frac{\delta^2 F}{\delta n^2}, \qquad (20)$$

$$K^{(3)}_{\boldsymbol{r}\boldsymbol{r}'\boldsymbol{r}''} = \frac{\delta^3 F}{\delta n(\boldsymbol{r}) \delta n(\boldsymbol{r}') \delta n(\boldsymbol{r}'')} = \frac{\delta^3 F}{\delta n^3}, \qquad (21)$$

$$K^{(4)}_{\boldsymbol{r},\boldsymbol{r}',\boldsymbol{r}'',\boldsymbol{r}'''} = \frac{\delta^4 F}{\delta n(\boldsymbol{r}) \delta n(\boldsymbol{r}') \delta n(\boldsymbol{r}'') n(\boldsymbol{r}''')} = \frac{\delta^4 F}{\delta n^4}. \qquad (22)$$

The implicit integration convention for the repeated lower indices can be illustrated by the following example:

$$K^{(2)}_{\boldsymbol{r}\boldsymbol{r}'} n^{(2)}_{\boldsymbol{r}} n^{(1)}_{\boldsymbol{r}'} \doteq \int \int d\boldsymbol{r} d\boldsymbol{r}' K^{(2)}(\boldsymbol{r},\boldsymbol{r}') n^{(2)}(\boldsymbol{r}) n^{(1)}(\boldsymbol{r}'). \qquad (23)$$

In some of the forthcoming equations, an explicit (but symbolic) indication of the functional derivatives, $\delta^n F / \delta n^n$, will be preferred to the shorthand $K^{(n)}_{\boldsymbol{r},\ldots,\boldsymbol{r}'\boldsymbol{r}''}$ notation. Explicit low-order terms of the λ expansion of the functional are given in Appendix A.

In an analogous manner, the power series of the potential $\omega_{\boldsymbol{r}}(\lambda)$,

$$\omega_{\boldsymbol{r}}(\lambda) = \sum_{m=0}^{\infty} \lambda^m \omega_{\boldsymbol{r}}^{(m)}, \qquad (24)$$

can be obtained as the functional derivative of $F[n]$, i.e.,

$$\omega_{\boldsymbol{r}_1}(\lambda) = \omega_{\boldsymbol{r}_1}^{(0)} + \sum_{k=1}^{\infty} \frac{1}{k!} K^{(k+1)}_{\boldsymbol{r}_1,\ldots,\boldsymbol{r}_{k+1}} \prod_{p=2}^{k+1} \Delta n_{\boldsymbol{r}_p}(\lambda), \qquad (25)$$

and the corresponding kth-order potential is given by the following general expression:

$$\omega_{\boldsymbol{r}_1}^{(k)} = \sum_{m=1}^{k} \frac{1}{m!} K^{(m+1)}_{\boldsymbol{r}_1,\ldots,\boldsymbol{r}_{m+1}} \sum_{j_1=2}^{k} \cdots \sum_{j_m=2}^{k} \prod_{p=2}^{m+1} n_{\boldsymbol{r}_p}^{(j_p)} \delta\left(k - \sum_{p=2}^{m+1} j_p \right). \qquad (26)$$

The lowest-order explicit formulas can be found in Appendix A.

The kth-order potential operator $\hat{\Omega}^{(k)} = \omega_{\boldsymbol{r}}^{(k)} \hat{n}_{\boldsymbol{r}}$ contains always a contribution of kth-order charge-density correction, according to the following general scheme:

$$\hat{\Omega}^{(k)} = \hat{\Omega}^{(\bar{k})} + \hat{n}_{\boldsymbol{r}} K^{(2)}_{\boldsymbol{r}\boldsymbol{r}'} n^{(k)}_{\boldsymbol{r}'}, \qquad (27)$$

where all the terms that contain lower than kth-order density correction contributions have been collected in $\hat{\Omega}^{(\bar{k})}$. The kth-order contribution to the expectation value of the potential operator consists in a sum of integrals of the mth-order potential and the $(k-m)$th-order charge density,

$$\langle \hat{\Omega} \rangle^{(k)} = \sum_{m=0}^{k} \omega_{\boldsymbol{r}}^{(m)} n_{\boldsymbol{r}}^{(k-m)}, \qquad (28)$$

which can be evaluated by the general expression

$$\langle \hat{\Omega} \rangle^{(k)} = \omega_{\boldsymbol{r}}^{(0)} n_{\boldsymbol{r}}^{(k)} + \omega_{\boldsymbol{r}}^{(k)} n_{\boldsymbol{r}}^{(0)} + \sum_{m=2}^{k} \frac{1}{(m-1)!} K^{(m)}_{\boldsymbol{r}_1,\ldots,\boldsymbol{r}_m} \sum_{j_1=1}^{k-1} \cdots \sum_{j_m=1}^{k-1} \prod_{p=1}^{m} n_{\boldsymbol{r}_p}^{(j_p)} \delta\left(k - \sum_{p=1}^{m} j_p \right). \qquad (29)$$

Finally, combining the expansions of the functional and the expectation value of the potential operator, the double count correction of the kth order is obtained as

$$F^{(k)} - \langle\hat{\Omega}\rangle^{(k)} = -\omega_{\boldsymbol{r}}^{(k)} n_{\boldsymbol{r}}^{(0)} - \sum_{m=2}^{k}\frac{m-1}{m!}K^{(m)}_{\boldsymbol{r}_1,\ldots,\boldsymbol{r}_m} \times \sum_{j_1=1}^{k-1}\cdots\sum_{j_m=1}^{k-1}\prod_{p=1}^{m} n_{\boldsymbol{r}_p}^{(j_p)}\,\delta\!\left(k-\sum_{p=1}^{m} j_p\right). \tag{30}$$

D. Perturbational solution of the effective Schrödinger equation

1. Expansion and eigenvalue corrections

The effective Schrödinger equation

$$\{\hat{H}^{(0)} + \lambda\hat{W} + \hat{\Omega}[n_{\Psi}]\}|\Psi\rangle = \mathcal{E}|\Psi\rangle \tag{31}$$

can be expanded in power series of the perturbational parameter λ using the Taylor expansions of the eigenvalue, $\mathcal{E}$, the eigenfunction, Ψ, and of the potential operator, $\hat{\Omega}$,

$$\mathcal{E} = \sum_{\nu=0}^{\infty}\lambda^{\nu}\mathcal{E}^{(\nu)}, \tag{32}$$

$$|\Psi\rangle = \sum_{\nu=0}^{\infty}\lambda^{\nu}|\Psi^{(\nu)}\rangle, \tag{33}$$

$$\hat{\Omega} = \sum_{\nu=0}^{\infty}\lambda^{\nu}\hat{\Omega}^{(\nu)}, \tag{34}$$

leading to

$$\sum_{\nu=0}^{\infty}\lambda^{\nu}\left\{\hat{H}^{(0)} + \lambda\hat{W} + \sum_{\tau=0}^{\infty}\lambda^{\tau}\hat{\Omega}^{(\tau)}\right\}|\Psi^{(\nu)}\rangle = \sum_{\nu=0}^{\infty}\sum_{\tau=0}^{\infty}\lambda^{\tau+\nu}\mathcal{E}^{(\tau)}|\Psi^{(\nu)}\rangle. \tag{35}$$

After regrouping the terms in the same power of λ, one obtains at the zeroth order

$$\{\hat{H}^{(0)} + \hat{\Omega}^{(0)}\}|\Psi^{(0)}\rangle = \mathcal{E}^{(0)}|\Psi^{(0)}\rangle. \tag{36}$$

For the general *k*th order,

$$\{\hat{H}^{(0)} + \hat{\Omega}^{(0)} - \mathcal{E}^{(0)}\}|\Psi^{(k)}\rangle + \hat{W}|\Psi^{(k-1)}\rangle = \sum_{\tau=1}^{k}\{\mathcal{E}^{(\tau)} - \hat{\Omega}^{(\tau)}\}|\Psi^{(k-\tau)}\rangle. \tag{37}$$

The *k*th-order eigenvalue correction is obtained after multiplication of the *k*th-order equation by $\langle\Psi^{(0)}|$

$$\mathcal{E}^{(k)} = \langle\Psi^{(0)}|\hat{W}|\Psi^{(k-1)}\rangle + \sum_{\tau=1}^{k}\langle\Psi^{(0)}|\hat{\Omega}^{(\tau)}|\Psi^{(k-\tau)}\rangle. \tag{38}$$

It should be recalled that the presence of a *k*th-order contribution from $\hat{\Omega}^{(k)}$ ($\tau=k$ in the summation) requires the knowledge of the *k*th-order wave function.

2. Wave-function corrections

A convenient way to express the eigenfunction corrections consists in introducing the reduced resolvent, $\hat{R}_0$, defined by the equation

$$\hat{R}_0\{\hat{H}^{(0)} + \hat{\Omega}^{(0)} - \mathcal{E}^{(0)}\} = 1 - |\Psi^{(0)}\rangle\langle\Psi^{(0)}|, \tag{39}$$

and the *k*th-order wave-function correction is obtained by applying the reduced resolvent to the *k*th-order equation, leading to

$$|\Psi^{(k)}\rangle = -\hat{R}_0\hat{W}|\Psi^{(k-1)}\rangle - \hat{R}_0\sum_{\tau=1}^{k}\{\hat{\Omega}^{(\tau)} - \mathcal{E}^{(\tau)}\}|\Psi^{(k-\tau)}\rangle. \tag{40}$$

Using that $\hat{R}_0|\Psi^{(0)}\rangle=0$, the first- and second-order wave-function corrections are, respectively,

$$|\Psi^{(1)}\rangle = -\hat{R}_0\{\hat{W} + \hat{\Omega}^{(1)}\}|\Psi^{(0)}\rangle, \tag{41}$$

$$|\Psi^{(2)}\rangle = -\hat{R}_0\{\hat{W} + \hat{\Omega}^{(1)} - \langle\hat{W} + \hat{\Omega}^{(1)}\rangle\}|\Psi^{(1)}\rangle - \hat{R}_0\hat{\Omega}^{(2)}|\Psi^{(0)}\rangle, \tag{42}$$

where $\langle\hat{W}+\hat{\Omega}^{(1)}\rangle=\langle\Psi^{(0)}|\hat{W}+\hat{\Omega}^{(1)}|\Psi^{(0)}\rangle$.

Although it is not immediately obvious, one should realize that the *k*th-order wave-function corrections must be determined self-consistently, because the *k*th-order potential $\hat{\Omega}^{(k)}$ depends on $|\Psi^{(k)}\rangle$. For instance, consider the expansion of the *k*th-order potential operator, $\hat{\Omega}^{(k)}$, in the following form, cf. Eqs. (13) and (28):

$$\hat{\Omega}^{(k)} = \hat{\Omega}^{(\bar{k})} + \int\int d\boldsymbol{r}d\boldsymbol{r}'\,\hat{n}(\boldsymbol{r})K^{(2)}(\boldsymbol{r},\boldsymbol{r}')\{\langle\Psi^{(0)}|\hat{n}(\boldsymbol{r}')|\Psi^{(k)}\rangle + \langle\Psi^{(k)}|\hat{n}(\boldsymbol{r}')|\Psi^{(0)}\rangle\}, \tag{43}$$

where $\hat{\Omega}^{(\bar{k})}$ collects all the contributions that come from wave-function corrections of order inferior to *k*. Since $K^{(2)}(\boldsymbol{r},\boldsymbol{r}')=K^{(2)}(\boldsymbol{r}',\boldsymbol{r})$ and $\langle\Psi^{(0)}|\hat{n}(\boldsymbol{r}')|\Psi^{(k)}\rangle=\langle\Psi^{(k)}|\hat{n}(\boldsymbol{r}')|\Psi^{(0)}\rangle$, the second term can be rewritten as $2\int\int d\boldsymbol{r}d\boldsymbol{r}'\,\hat{n}(\boldsymbol{r})K^{(2)}(\boldsymbol{r},\boldsymbol{r}')\langle\Psi^{(0)}|\hat{n}(\boldsymbol{r}')|\Psi^{(k)}\rangle$. Introducing the effective interaction operator, $\hat{G}_0$,

$$\hat{G}_0 = 2\int\int d\boldsymbol{r}d\boldsymbol{r}'\,\hat{n}(\boldsymbol{r})|\Psi^{(0)}\rangle K^{(2)}(\boldsymbol{r},\boldsymbol{r}')\langle\Psi^{(0)}|\hat{n}(\boldsymbol{r}'), \tag{44}$$

one arrives at the following simple form of Eq. (43):

$$\hat{\Omega}^{(k)}|\Psi^{(0)}\rangle = \hat{\Omega}^{(\bar{k})}|\Psi^{(0)}\rangle + \hat{G}_0|\Psi^{(k)}\rangle. \tag{45}$$

Substituting Eq. (45) in the *k*th-order wave-function correction, the nonlinearity becomes obvious through the presence of the last term, containing $\Psi^{(k)}$,

$$|\Psi^{(k)}\rangle = -\hat{R}_0\hat{W}|\Psi^{(k-1)}\rangle - \hat{R}_0\sum_{\tau=1}^{k-1}\{\hat{\Omega}^{(\tau)}-\mathcal{E}^{(\tau)}\}|\Psi^{(k-\tau)}\rangle - \hat{R}_0\hat{\Omega}^{(\bar{k})}|\Psi^{(0)}\rangle - \hat{R}_0\hat{G}_0|\Psi^{(k)}\rangle. \tag{46}$$

Application of the above expression to the first-order wave-function correction leads to

$$|\Psi^{(1)}\rangle = -\hat{R}_0\hat{W}|\Psi^{(0)}\rangle - \hat{R}_0\hat{G}_0|\Psi^{(1)}\rangle, \tag{47}$$

which can be formally rearranged by introducing an *effective screening factor*, $(1+\hat{R}_0\hat{G}_0)^{-1}$, as

$$|\Psi^{(1)}\rangle = -(1+\hat{R}_0\hat{G}_0)^{-1}\hat{R}_0\hat{W}|\Psi^{(0)}\rangle. \tag{48}$$

Using the series expansion of the effective screening factor, one obtains

$$|\Psi^{(1)}\rangle = -\sum_{n=0}^{\infty}(-\hat{R}_0\hat{G}_0)^n\hat{R}_0\hat{W}|\Psi^{(0)}\rangle, \tag{49}$$

where the sum can be constructed by recursion.

In a similar manner, the second-order wave-function correction is seen to satisfy the following self-consistent equation:

$$|\Psi^{(2)}\rangle = -\hat{R}_0(\hat{W}+\hat{\Omega}^{(1)}-\langle\hat{W}+\hat{\Omega}^{(1)}\rangle|\Psi^{(1)}\rangle - \hat{R}_0\hat{\Omega}^{(\bar{2})}|\Psi^{(0)}\rangle - \hat{R}_0\hat{G}_0|\Psi^{(2)}\rangle\ , \tag{50}$$

which can be formally solved as

$$|\Psi^{(2)}\rangle = -(1+\hat{R}_0\hat{G}_0)^{-1}\hat{R}_0\{\hat{W}+\hat{\Omega}^{(1)}-\langle\hat{W}+\hat{\Omega}^{(1)}\rangle\}|\Psi^{(1)}\rangle - (1+\hat{R}_0\hat{G}_0)^{-1}\hat{R}_0\hat{\Omega}^{(\bar{2})}|\Psi^{(0)}\rangle. \tag{51}$$

Here $\hat{\Omega}^{(\bar{2})}$ denotes the part of the second-order potential operator that is independent of the second-order wave-function correction,

$$\hat{\Omega}^{(\bar{2})} = \int\int d\boldsymbol{r}d\boldsymbol{r}'\hat{n}(\boldsymbol{r})K^{(2)}(\boldsymbol{r},\boldsymbol{r}')\langle\Psi^{(1)}|\hat{n}(\boldsymbol{r}')-n^{(0)}(\boldsymbol{r}')|\Psi^{(1)}\rangle + \frac{1}{2}\int\int\int d\boldsymbol{r}d\boldsymbol{r}'d\boldsymbol{r}''\hat{n}(\boldsymbol{r})K^{(3)}(\boldsymbol{r},\boldsymbol{r}',\boldsymbol{r}'')n^{(1)}(\boldsymbol{r}')n^{(1)}(\boldsymbol{r}''). \tag{52}$$

In fact, the effective screening factor, $(1+\hat{R}_0\hat{G}_0)^{-1}$, that handles formally the nonlinearity, occurs in the same form in all orders. Introducing the notation $\Psi^{(\bar{k})}$ for the wave-function correction of order inferior to k,

$$\Psi^{(\bar{k})} = -\hat{R}_0\hat{W}|\Psi^{(k-1)}\rangle - \hat{R}_0\sum_{\tau=1}^{k-1}(\hat{\Omega}^{(\tau)}-\mathcal{E}^{(\tau)})|\Psi^{(k-\tau)}\rangle - \hat{R}_0\hat{\Omega}^{(\bar{k})}|\Psi^{(0)}\rangle, \tag{53}$$

the kth-order wave-function correction satisfies an equation of the following general form:

$$|\Psi^{(k)}\rangle = -\sum_{n=0}^{\infty}(-\hat{R}_0\hat{G}_0)^n|\Psi^{(\bar{k})}\rangle, \tag{54}$$

where the iterative calculation of the infinite sum can probably be truncated at a low value of n.

Remark that in the first-order case, Eq. (37) becomes

$$(\hat{H}^{(0)}+\hat{\Omega}^{(0)}-\mathcal{E}^{(0)})|\Psi^{(1)}\rangle = -\{\hat{W}+\hat{\Omega}^{(1)}-\mathcal{E}^{(1)}\}|\Psi^{(0)}\rangle, \tag{55}$$

and it can be considered as the many-body analog of the generalized Sternheimer equation [51–53].

III. PERTURBATIONAL CORRECTIONS TO THE TOTAL ENERGY

The kth-order total energy correction is given by the sum of the eigenvalue, Eq. (38), and double count Eq. (30) corrections. The last term in the sum of the eigenvalue correction, $\langle\Psi^{(0)}|\hat{\Omega}^{(k)}|\Psi^{(0)}\rangle$, cancels with the term $\omega_r^{(k)}n_r^{(0)}$ in the double count correction, and we have

$$E^{(k)} = \langle\Psi^{(0)}|\hat{W}|\Psi^{(k-1)}\rangle + \sum_{\nu=1}^{k-1}\langle\Psi^{(0)}|\hat{\Omega}^{(\nu)}|\Psi^{(k-\nu)}\rangle + E_F^{(k)}, \tag{56}$$

where $E_F^{(k)}=F^{(k)}-\langle\hat{\Omega}\rangle^{(k)}+\omega_r^{(k)}n_r^{(0)}$ collects all the "functional-dependent" contributions.

This total energy expression is in contradiction with Wigner's $(2n+1)$ rule, which tells that energy corrections of order $2n$ and $2n+1$ are fully determined by the wave-function corrections up to order n [6,33]. While it can be expected that the $(2n+1)$-rule violating terms involving the density functional and its derivatives cancel each other, the matrix elements of the perturbation operator $\hat{W}$ depending on the wave-function corrections up to order $k-1$ should be converted to another form, which does not contradict Wigner's $(2n+1)$ rule. Such a turnover transformation [28,54–56] of the matrix elements has been derived for a nonlinear Schrödinger equation in Ref. [33] as

$$\langle\Psi^{(0)}|\hat{W}|\Psi^{(p)}\rangle = \langle\Psi^{(m)}|\hat{W}|\Psi^{(p-m)}\rangle + \sum_{j=1}^{m}\langle\Psi^{(p+1-j)}|\mathcal{E}^{(j)}-\hat{\Omega}^{(j)}|\Psi^{(0)}\rangle - \sum_{j=1}^{m}\sum_{\nu=0}^{p-m}\langle\Psi^{(j)}|\mathcal{E}^{(p+1-j-\nu)}-\hat{\Omega}^{(p+1-j-\nu)}|\Psi^{(\nu)}\rangle. \tag{57}$$

Applied to the kth-order energy correction, Eq. (56), the turnover expression leads to the following form of the total energy correction:

$$
\begin{aligned}
E^{(k,m)} &= \langle \Psi^{(m)} | \hat{W} | \Psi^{(k-m-1)} \rangle \\
&\quad + \sum_{j=1}^{m} \langle \Psi^{(j)} | \hat{\Omega}^{(k-j)} | \Psi^{(0)} \rangle + \sum_{j=m+1}^{k-1} \langle \Psi^{(k-j)} | \hat{\Omega}^{(j)} | \Psi^{(0)} \rangle \\
&\quad - \sum_{j=1}^{m} \sum_{\nu=1}^{k-m-1} \langle \Psi^{(j)} | \mathcal{E}^{(k-j-\nu)} - \hat{\Omega}^{(k-j-\nu)} | \Psi^{(\nu)} \rangle + E_F^{(k)},
\end{aligned}
\tag{58}
$$

where $m < k$ indicates the number of times the basic turnover transformation has been applied.

Explicit total energy corrections for even $(2n)$ and odd $(2n+1)$ orders can be obtained by setting $m=n$ and $k=2n$ or $k=2n+1$,

$$
\begin{aligned}
E^{(2n)} &= \langle \Psi^{(n-1)} | \hat{W} | \Psi^{(n)} \rangle + \sum_{j=1}^{n} \langle \Psi^{(j)} | \hat{\Omega}^{(2n-j)} | \Psi^{(0)} \rangle \\
&\quad + \sum_{j=n+1}^{2n-1} \langle \Psi^{(j)} | \hat{\Omega}^{(2n-j)} | \Psi^{(0)} \rangle \\
&\quad + \sum_{j=1}^{n} \sum_{\nu=1}^{n-1} \left(\langle \Psi^{(j)} | \hat{\Omega}^{(2n-j-\nu)} | \Psi^{(\nu)} \rangle - \mathcal{E}^{(2n-j-\nu)} \langle \Psi^{(j)} | \Psi^{(\nu)} \rangle \right) \\
&\quad + E_F^{(2n)},
\end{aligned}
\tag{59}
$$

$$
\begin{aligned}
E^{(2n+1)} &= \langle \Psi^{(n)} | \hat{W} | \Psi^{(n)} \rangle + \sum_{j=1}^{n} \langle \Psi^{(j)} | \hat{\Omega}^{(2n+1-j)} | \Psi^{(0)} \rangle \\
&\quad + \sum_{j=n+1}^{2n} \langle \Psi^{(j)} | \hat{\Omega}^{(2n+1-j)} | \Psi^{(0)} \rangle \\
&\quad + \sum_{j=1}^{n} \sum_{\nu=1}^{n} \left(\langle \Psi^{(j)} | \hat{\Omega}^{(2n+1-j-\nu)} | \Psi^{(\nu)} \rangle - \mathcal{E}^{(2n+1-j-\nu)} \langle \Psi^{(j)} | \Psi^{(\nu)} \rangle \right) \\
&\quad + E_F^{(2n+1)}.
\end{aligned}
\tag{60}
$$

Further cancelations are expected on the basis of the general $(2n+1)$ rule. However, they seem to be difficult to formalize in a general way, for instance between the functional contribution $E_F^{(2n)}$ and the higher-order Ω contributions. They will be treated in a case-by-case manner, by discussing the lowest-order total energy expressions up to order 4.

A. Zeroth order

The zeroth-order total energy expression obtained directly from Eq. (56),

$$
E^{(0)} = \mathcal{E}^{(0)} - \frac{\delta F}{\delta n_r} n_r^{(0)} + F[n^{(0)}],
\tag{61}
$$

is the sum of the eigenvalue, $\mathcal{E}^{(0)}$, and of the zeroth-order double count correction.

B. First order

At first order, the general formula, Eq. (56), provides

$$
\begin{aligned}
E^{(1)} &= \langle \Psi^{(0)} | \hat{W} | \Psi^{(0)} \rangle + \langle \Psi^{(0)} | \hat{\Omega}^{(1)} | \Psi^{(0)} \rangle \\
&\quad - \frac{\delta^2 F}{\delta n_r \delta n_{r'}} n_r^{(1)} n_{r'}^{(0)} - \frac{\delta F}{\delta n_r} n_r^{(1)} + \frac{\delta F}{\delta n_r} n_r^{(1)},
\end{aligned}
\tag{62}
$$

where, like in Eq. (61), the implicit integration convention is used for the repeated lower indices. It is easy to see that the $\langle \Psi^{(0)} | \hat{\Omega}^{(1)} | \Psi^{(0)} \rangle$ term in the eigenvalue correction is canceled by the $\omega_r^{(1)} n_r^{(0)} = (\delta^2 F / \delta n_r \delta n_{r'}) n_r^{(1)} n_{r'}^{(0)}$ term of the potential, while the $\delta F / \delta n_r n_r^{(1)} = \omega_r^{(0)} n_r^{(1)}$ contributions to the functional and the potential cancel each other trivially. Thus one obtains the "conventional" energy correction,

$$
E^{(1)} = \langle \Psi^{(0)} | \hat{W} | \Psi^{(0)} \rangle,
\tag{63}
$$

i.e., the expectation value of the perturbation operator with the zeroth-order wave function. This result is a generalization of the Hellman-Feynman theorem and it is a consequence of the variational character of the solution of the zeroth-order Schrödinger equation.

C. Second order

The general expression, Eq. (56), applied to the second order leads to

$$
\begin{aligned}
E^{(2)} &= \langle \Psi^{(0)} | \hat{W} | \Psi^{(1)} \rangle + \langle \Psi^{(0)} | \hat{\Omega}^{(1)} | \Psi^{(1)} \rangle \\
&\quad - \frac{1}{2} \frac{\delta^2 F}{\delta n_r \delta n_{r'}} n_r^{(1)} n_{r'}^{(1)}.
\end{aligned}
\tag{64}
$$

Using the explicit form (A6) of the first-order potential, $\omega^{(1)}$, and remembering the form of the first-order density correction, Eq. (10), it can be seen immediately that the second and the third terms of Eq. (64) cancel each other, i.e.,

$$
\langle \Psi^{(0)} | \hat{\Omega}^{(1)} | \Psi^{(1)} \rangle - \frac{1}{2} \frac{\delta^2 F}{\delta n_r \delta n_{r'}} n_r^{(1)} n_{r'}^{(1)} = 0,
\tag{65}
$$

and finally one is left with an apparently "conventional" form of the second-order energy correction,

$$
E^{(2)} = \langle \Psi^{(0)} | \hat{W} | \Psi^{(1)} \rangle.
\tag{66}
$$

This expression is equivalent to Eq. (131) of Ref. [5] as far as the external perturbation is considered to contain a linear contribution only.

It should be kept in mind that the first-order wave-function correction $|\Psi^{(1)}\rangle$ itself is obtained from the solution of the self-consistent equation, Eq. (47), which means that in general the nonlinearity of the problem appears already at this order of the perturbation.

D. Third-order correction

Third- and higher-order total energy corrections can be obtained after the application of the turnover relationship, i.e., from Eqs. (59) or (60), and handle the remaining $(2n+1)$-rule violating contributions individually. For instance, in the third-order case one obtains from Eq. (60)

$$\begin{aligned} E^{(3)} = {} & \langle\Psi^{(1)}|\hat{W}+\hat{\Omega}^{(1)}|\Psi^{(1)}\rangle \\ & - \mathcal{E}^{(1)}\langle\Psi^{(1)}|\Psi^{(1)}\rangle \\ & + \langle\Psi^{(1)}|\hat{\Omega}^{(2)}|\Psi^{(0)}\rangle \\ & + \langle\Psi^{(0)}|\hat{\Omega}^{(2)}|\Psi^{(1)}\rangle \\ & - \frac{1}{3}\frac{\delta^3 F}{\delta n_{\mathbf{r}}\delta n_{\mathbf{r}'}\delta n_{\mathbf{r}''}} n_{\mathbf{r}}^{(1)} n_{\mathbf{r}'}^{(1)} n_{\mathbf{r}''}^{(1)} - \frac{\delta^2 F}{\delta n_{\mathbf{r}}\delta n_{\mathbf{r}'}} n_{\mathbf{r}}^{(1)} n_{\mathbf{r}'}^{(2)}. \end{aligned} \quad (67)$$

After a series of relatively straightforward transformations and using the definition of $\mathcal{E}^{(1)}$ and $\hat{\Omega}^{(2)}$, as detailed in Appendix B, the final third-order expression

$$E^{(3)} = E_W^{(3)} + E_{\Omega^{(1)}}^{(3)} + E_{F^{(3)}}^{(3)} \quad (68)$$

is split into three components, each having a well-defined physical origin.

The first contribution, $E_W^{(3)}$, has the form of the usual third-order RSPT correction,

$$E_W^{(3)} = \langle\Psi^{(1)}|\hat{W} - \langle\hat{W}\rangle|\Psi^{(1)}\rangle, \quad (69)$$

calculated with the self-consistently determined first-order eigenfunction correction of Eq. (47).

There is an analogous term, $E_{\Omega^{(1)}}^{(3)}$, which is due to the first-order shift of the density-dependent potential operator,

$$E_{\Omega^{(1)}}^{(3)} = \langle\Psi^{(1)}|\hat{\Omega}^{(1)} - \langle\hat{\Omega}^{(1)}\rangle|\Psi^{(1)}\rangle. \quad (70)$$

The third contribution, $E_{F^{(3)}}^{(3)}$, involves the functional explicitly as

$$E_{F^{(3)}}^{(3)} = \frac{1}{6}\frac{\delta^3 F}{\delta n_{\mathbf{r}}\delta n_{\mathbf{r}'}\delta n_{\mathbf{r}''}} n_{\mathbf{r}}^{(1)} n_{\mathbf{r}'}^{(1)} n_{\mathbf{r}''}^{(1)}. \quad (71)$$

In the special case of one-electron perturbations of a noninteracting Kohn-Sham system, i.e., $F[n]=E_{\mathrm{Hxc}}[n]$, Eq. (68) is similar to the third-order DFPT expression obtained by Gonze and Vigneron [4], and it is equivalent to Eq. (112) of Gonze [6] provided that the perturbation does not influence the form of the local potential explicitly.

E. Fourth-order correction

The fourth-order energy correction, obtained directly from the general formula, Eq. (59), reads

$$\begin{aligned} E^{(4)} = {} & \langle\Psi^{(1)}|\hat{W}|\Psi^{(2)}\rangle + \langle\Psi^{(1)}|\hat{\Omega}^{(1)}|\Psi^{(2)}\rangle + \langle\Psi^{(1)}|\hat{\Omega}^{(3)}|\Psi^{(0)}\rangle \\ & + \langle\Psi^{(0)}|\hat{\Omega}^{(3)}|\Psi^{(1)}\rangle + \langle\Psi^{(0)}|\hat{\Omega}^{(2)}|\Psi^{(2)}\rangle + \langle\Psi^{(1)}|\hat{\Omega}^{(2)}|\Psi^{(1)}\rangle \\ & - \mathcal{E}^{(2)}\langle\Psi^{(1)}|\Psi^{(1)}\rangle - \mathcal{E}^{(1)}\langle\Psi^{(1)}|\Psi^{(2)}\rangle \\ & - \frac{1}{8}\frac{\delta^4 F}{\delta n^4} n^{(1)} n^{(1)} n^{(1)} n^{(1)} - \frac{\delta^3 F}{\delta n^3} n^{(1)} n^{(1)} n^{(2)} \\ & - \frac{1}{2}\frac{\delta^2 F}{\delta n^2} n^{(2)} n^{(2)} - \frac{\delta^2 F}{\delta n^2} n^{(1)} n^{(3)}. \end{aligned} \quad (72)$$

After substitution of the first- and second-order eigenvalue corrections and using the explicit expressions of the potential operators, $\hat{\Omega}^{(2)}$ and $\hat{\Omega}^{(3)}$, two alternative versions of the fourth-order total energy correction, both in full harmony with the $(2n+1)$ rule, can be derived, as shown in Appendix C. Both of these expressions contain a conventional fourth-order term, due to the perturbation operator on the one hand, and to the first-order shift of the potential operator on the other,

$$E_W^{(4)} = \langle\Psi^{(1)}|\hat{W} - \langle\hat{W}\rangle|\Psi^{(2)}\rangle - \langle\Psi^{(0)}|\hat{W}|\Psi^{(1)}\rangle\langle\Psi^{(1)}|\Psi^{(1)}\rangle, \quad (73)$$

$$E_{\Omega^{(1)}}^{(4)} = \langle\Psi^{(1)}|\hat{\Omega}^{(1)} - \langle\hat{\Omega}^{(1)}\rangle|\Psi^{(2)}\rangle - \langle\Psi^{(0)}|\hat{\Omega}^{(1)}|\Psi^{(1)}\rangle\langle\Psi^{(1)}|\Psi^{(1)}\rangle, \quad (74)$$

as well as specific nonlinear terms.

According to the first variant, one of the contributions is due to the second-order potential operator,

$$E_{\Omega^{(2)}}^{(4)} = \langle\Psi^{(0)}|\hat{\Omega}^{(2)}|\Psi^{(2)}\rangle + \langle\Psi^{(1)}|\hat{\Omega}^{(2)} - \langle\hat{\Omega}^{(2)}\rangle|\Psi^{(1)}\rangle, \quad (75)$$

and another comes from the explicit functional terms,

$$E_{F^{(2,4)}}^{(4)} = \frac{1}{24}\frac{\delta^4 F}{\delta n^4} n^{(1)} n^{(1)} n^{(1)} n^{(1)} - \frac{1}{2}\frac{\delta^2 F}{\delta n^2} n^{(2)} n^{(2)}. \quad (76)$$

The total fourth-order correction is the sum of the above contributions,

$$E^{(4)} = E_W^{(4)} + E_{\Omega^{(1)}}^{(4)} + E_{\Omega^{(2)}}^{(4)} + E_{F^{(2,4)}}^{(4)}. \quad (77)$$

In another alternative variant of the fourth-order energy expression, the terms containing $\hat{\Omega}^{(2)}$ and the functional are regrouped in a different way, as explained in Appendix C. While the contributions $E_W^{(4)}$ and $E_{\Omega^{(1)}}^{(4)}$ remain the same, the last two contributions can be redefined as

$$E_{\Omega^{(2)'}}^{(4)} = -\langle\Psi^{(0)}|\hat{\Omega}^{(2)}|\Psi^{(2)}\rangle, \quad (78)$$

$$\begin{aligned} E_{F^{(2,3,4)}}^{(4)} = {} & \frac{1}{2}\frac{\delta^2 F}{\delta n^2} n^{(2)} n^{(2)} + \frac{1}{2}\frac{\delta^3 F}{\delta n^3} n^{(1)} n^{(1)} n^{(2)} \\ & + \frac{1}{24}\frac{\delta^4 F}{\delta n^4} n^{(1)} n^{(1)} n^{(1)} n^{(1)}, \end{aligned} \quad (79)$$

leading to

$$E^{(4)} = E_W^{(4)} + E_{\Omega^{(1)}}^{(4)} + E_{\Omega^{(2)'}}^{(4)} + E_{F^{(2,3,4)}}^{(4)}. \quad (80)$$

It should be noted that both forms of the fourth-order total energy expression contain at most second-order wave-function corrections. Equation (80) is equivalent to the fourth-order result of Ref. [5], disregarding $E_{\Omega^{(2)'}}^{(4)}$ contribution. This difference is a consequence of a different choice of the normalization convention for the wave function.

IV. EXAMPLES OF APPLICATION

The above derived energy and wave-function corrections are valid for arbitrary perturbations. In principle, they can be applied in the context of many-electron (multideterminant) zeroth-order wave functions, and one has a wide choice as far as the nature of the density functionals is concerned. In the case of one-electron perturbations applied to the Kohn-Sham independent particle system, one obtains the DFPT, essentially the same as derived by Gonze and others. For two-electron perturbations, like the long-range fluctuation potential in the context of the range-separated hybrid functionals applied to a zeroth-order Kohn-Sham determinant, the general results apply and one can retrieve and generalize earlier second-order results [14]. It should be recalled that the same framework can be adapted to other kinds of more general density-dependent functionals, such as those arising in quantum chemical solvent effect models. In fact, a first realization of the nonlinear RSPT has been worked out in a solvent effect context [20–22] and applied recently to the study of solvent effects on excited states [57]. It should also be mentioned that the present perturbational scheme can be applied to multiconfigurational zeroth-order problems. However, in such cases special attention should be paid to quasidegeneracy problems [58].

A. Coupled perturbed Kohn-Sham equations

The first example is the case of a time-independent one-electron perturbation $\hat{W}=\hat{V}=\int d\boldsymbol{r}\hat{\rho}(\boldsymbol{r})v(\boldsymbol{r})$ applied to an electronic system described by the conventional Kohn-Sham theory. The density functional, $F[n]=E_{\mathrm{Hxc}}[n]$, is the Hartree-exchange-correlation functional, and the unperturbed problem is the solution of the Kohn-Sham Hamiltonian, leading to the Kohn-Sham determinant, $|\Psi^{(0)}\rangle=|\Phi\rangle$. The perturbation can be a polarization under the effect of time-independent electric fields, the displacement of atoms, permitting the determination of the force constants, etc. The first-order wave-function correction can be expanded in terms of singly excited configurations generated from the Kohn-Sham determinant,

$$|\Psi^{(1)}\rangle = \sum_{ia} c_i^a |\Phi_i^a\rangle. \tag{81}$$

After substitution of the above form of the wave-function correction and the spectral expansion of the reduced resolvent $\hat{R}_0$ in terms of the excited eigenfunctions and eigenvalues of the Kohn-Sham Hamiltonian,

$$\hat{R}_0 = \sum_{I(\neq 0)} \frac{|\Phi_I\rangle\langle\Phi_I|}{\mathcal{E}_I-\mathcal{E}_0} = \sum_{ia}\frac{|\Phi_i^a\rangle\langle\Phi_i^a|}{\varepsilon_a-\varepsilon_i} + \sum_{ia}\sum_{jb}\frac{|\Phi_{ij}^{ab}\rangle\langle\Phi_{ij}^{ab}|}{\varepsilon_a+\varepsilon_b-\varepsilon_i-\varepsilon_j} + \cdots, \tag{82}$$

the first-order perturbation equation, Eq. (47), becomes

$$\sum_{ia} c_i^a|\Phi_i^a\rangle = -\sum_{kd}\frac{|\Phi_k^d\rangle\langle\Phi_k^d|\hat{V}|\Phi\rangle}{\varepsilon_d-\varepsilon_k} - 2\sum_{kd}\sum_{jb} c_j^b\frac{|\Phi_k^d\rangle\langle\Phi_k^d|\hat{n}_{\boldsymbol{r}}|\Phi\rangle K^{(2)}_{\boldsymbol{rr}'}\langle\Phi|\hat{n}_{\boldsymbol{r}'}|\Phi_j^b\rangle}{\varepsilon_d-\varepsilon_k}, \tag{83}$$

where ε_k and ε_d are occupied and virtual one-electron Kohn-Sham orbital energies, respectively. Note that only singly excited determinants contribute to the reduced resolvent, since both $\hat{V}$ and $\hat{n}_r$ are one-electron operators, which have vanishing matrix elements between the ground state and doubly excited Slater determinants.

After multiplication of the perturbation equation by $\langle\Phi_j^b|$, and taking into account the orthogonality of the orbitals, the following set of linear equations is obtained:

$$\sum_{bj}\left\{\delta_{ij}\delta_{ab}(\varepsilon_a-\varepsilon_i) + 2\int\int d\boldsymbol{r}d\boldsymbol{r}'\,\phi_i^*(\boldsymbol{r})\phi_a(\boldsymbol{r})K_{\mathrm{Hxc}}(\boldsymbol{r},\boldsymbol{r}') \times\phi_b^*(\boldsymbol{r}')\phi_j(\boldsymbol{r}')\right\}c_j^b = -\int d\boldsymbol{r}\,\phi_i^*(\boldsymbol{r})v(\boldsymbol{r})\phi_a(\boldsymbol{r}), \tag{84}$$

where the Hartree-exchange-correlation kernel, entering in the definition of the effective interaction operator, Eq. (44), is

$$K_{\mathrm{Hxc}}(\boldsymbol{r},\boldsymbol{r}') = \frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|} + \frac{\delta^2 E_{\mathrm{xc}}}{\delta n(\boldsymbol{r})\delta n(\boldsymbol{r}')}. \tag{85}$$

Denoting the quantity in curly brackets on the lhs of Eq. (84) as $A_{ia,jb}$, and the matrix element of the perturbation operator on the rhs by v_{ia}, the set of linear equations (84) can also be written as

$$\sum_{jb} A_{ia,jb}c_j^b = -v_{ia}, \tag{86}$$

which provides the second-order energy correction in terms of the inverse of the $A_{jb,ia}$ matrix,

$$E^{(2)} = -\sum_{jb}\sum_{ia} v_{jb}A^{-1}_{jb,ia}v_{ia}. \tag{87}$$

Recall that the A matrix can be calculated in various approximations. For instance, in the RPA (random phase approximation), which consists in neglecting the exchange-corelation (xc) contribution to the Hartree-exchange-correlation kernel, $K_{\mathrm{Hxc}}(\boldsymbol{r},\boldsymbol{r}')$, it reads

$$A^{\mathrm{RPA}}_{ia,jb} = \delta_{ij}\delta_{ab}(\varepsilon_a-\varepsilon_i) + 2\langle ab|ij\rangle, \tag{88}$$

where the notation $\langle ab|ij\rangle$ stands for the electron repulsion integral,

$$\langle ab|ij\rangle = \int\int d\boldsymbol{r}d\boldsymbol{r}'\,\varphi_a^*(\boldsymbol{r})\varphi_b^*(\boldsymbol{r}')|\boldsymbol{r}-\boldsymbol{r}'|^{-1}\varphi_i(\boldsymbol{r})\varphi_j(\boldsymbol{r}'). \tag{89}$$

Equation (88) is the standard form of the static DFT perturbation equations for real orbitals. Third- and fourth-order response equations can be worked out along similar lines to get first and second hyperpolarizabilities.

B. Long-range correlation corrections to range-separated hybrid functionals

A promising approach to overcome several difficulties in standard Kohn-Sham density-functional theory, related to the approximate nature of popular exchange-correlation functionals, is based on the hypothesis that while short-range electron interactions can be efficiently treated by a universal density functional, long-range exchange and correlation effects are better handled by explicit wave-function techniques [10,59,60]. This idea has led to a range-separated generalization of the Kohn-Sham method [11], where the noninteracting Kohn-Sham reference system is replaced by a "long-range-interacting" one, defined by the following total energy functional:

$$E^{\mu}=\min_{\Psi^{\mu}\to N}\{\langle\Psi^{\mu}|\hat{T}+\hat{V}_{ne}+\hat{W}^{\mathrm{lr},\mu}_{ee}|\Psi^{\mu}\rangle+E^{\overline{\mathrm{sr}},\mu}_{\mathrm{Hxc}}[n_{\Psi^{\mu}}]\}. \quad (90)$$

The short-range Hartree-exchange-correlation functional, appearing in Eq. (90), is defined as $E^{\overline{\mathrm{sr}},\mu}_{\mathrm{Hxc}}[n]=E_{\mathrm{Hxc}}[n]-E^{\mathrm{lr},\mu}_{\mathrm{Hxc}}[n]$ [11,14]. The total Hartree-exchange-correlation functional has been already given in Eqs. (3)–(5) and the long-range Hartree-exchange-correlation functional, $E^{\mathrm{lr},\mu}_{\mathrm{Hxc}}[n]$, is defined in an analogous manner by taking the difference of the universal long-range interacting functional,

$$F^{\mathrm{lr},\mu}_{\mathrm{HK}}[n]=\min_{\Psi\to n}\langle\Psi|\hat{T}+\hat{W}^{\mathrm{lr},\mu}_{ee}|\Psi\rangle, \quad (91)$$

and $T_s[n]$, Eq. (5). The notation $\overline{\mathrm{sr}}$ stresses the fact that the above-defined short-range correlation functional is "complementary" with respect to the purely long-range functional and, in addition to the short-range electron correlation, includes short-range—long-range coupling effects [61].

If the short-range Hartree-exchange-correlation functional, $E^{\overline{\mathrm{sr}},\mu}_{\mathrm{Hxc}}[n]$, were known exactly, the total energy, $E=E^{\mu}$, would be independent of the parameter μ, which controls the separation between the two components of the *e-e* interaction function, $w_{ee}(r)=w^{\mathrm{sr},\mu}_{ee}(r)+w^{\mathrm{lr},\mu}_{ee}(r)$ entering in the definition of the *e-e* interaction operators, $\hat{W}_{ee}=\int\int d\boldsymbol{r}_1 d\boldsymbol{r}_2 w_{ee}(|\boldsymbol{r}_2-\boldsymbol{r}_1|)\hat{n}_2(\boldsymbol{r}_1,\boldsymbol{r}_2)$, with $\hat{n}_2(\boldsymbol{r}_1,\boldsymbol{r}_2)$ the operator of the pair density. There are several possibilities to realize the long-range–short-range separation of the Coulomb interaction [62], e.g., by the error function, $w^{\mathrm{lr},\mu}_{ee}(r)=\mathrm{erf}(\mu r)/r$, but this particular detail does not influence the forthcoming perturbational results, which are valid for arbitrary partitioning of the *e-e* interaction.

In the following, the perturbation theory will be applied for the treatment of the long-range correlation effects. The zeroth-order reference state, Φ^{μ}, will be a single determinant obtained by the self-consistent solution of the Kohn-Sham equations with the range-separated hybrid (RSH) functional [14], where long-range exchange effects are described in a Hartree-Fock-like manner. It will be shown that the second-order result, described earlier [14], can be obtained as a special case of the general theory outlined in the preceding sections. The main features of higher-order generalizations will be discussed as well. For the sake of notational simplicity, the superscript μ, referring to the range-separation parameter, will be omitted in the forthcoming expressions.

The minimizing wave function Ψ in Eq. (90) is provided by the Euler-Lagrange (effective Schrödinger) equation [cf. Eq. (2)],

$$(\hat{T}+\hat{V}_{ne}+\hat{V}^{\mathrm{lr}}_{\mathrm{Hx,HF}}[\Phi]+\lambda\hat{\mathcal{W}}^{\mathrm{lr}}+\hat{V}^{\overline{\mathrm{sr}}}_{\mathrm{Hxc}}[n_{\Psi}])|\Psi\rangle=\mathcal{E}|\Psi\rangle. \quad (92)$$

For $\lambda=1$, the physical energy is recovered, while for $\lambda=0$, Eq. (92) reduces to the range-separated hybrid model: $\Psi(\lambda=0)=\Phi$.

The perturbation, $\hat{\mathcal{W}}^{\mathrm{lr}}$, switched on by a formal coupling constant λ,

$$\hat{\mathcal{W}}^{\mathrm{lr}}=\hat{W}^{\mathrm{lr}}_{ee}-\hat{V}^{\mathrm{lr}}_{\mathrm{Hx,HF}}[\Phi], \quad (93)$$

is the long-range fluctuation potential operator, defined as the difference between the exact long-range electron interaction operator and its mean-field (Hartree-Fock-type) approximation. The following correspondences can be established with the general RSPT scheme:

$$F[n]=E^{\overline{\mathrm{sr}}}_{\mathrm{Hxc}}[n_{\Psi}], \quad (94)$$

$$\hat{\Omega}[n_{\Psi}]=\hat{V}^{\overline{\mathrm{sr}}}_{\mathrm{Hxc}}[n_{\Psi}], \quad (95)$$

$$\hat{W}=\hat{\mathcal{W}}^{\mathrm{lr}}=\hat{W}^{\mathrm{lr}}_{ee}-\hat{V}^{\mathrm{lr}}_{\mathrm{Hx,HF}}[\Phi]. \quad (96)$$

The zeroth-order energy is the sum of the Kohn-Sham orbital energies plus the double count correction due to the short-range Hartree-exchange-correlation functional,

$$E^{(0)}=\sum_{k}^{\mathrm{occ}}\varepsilon_k-\int d\boldsymbol{r}\, n_{\Phi}(\boldsymbol{r})v^{\overline{\mathrm{sr}}}_{\mathrm{Hxc}}(\boldsymbol{r})[n_{\Phi}]+E^{\overline{\mathrm{sr}}}_{\mathrm{Hxc}}[n_{\Phi}], \quad (97)$$

while the first-order correction,

$$E^{(1)}=\langle\Phi|\hat{W}^{\mathrm{lr}}_{ee}-\hat{V}^{\mathrm{lr}}_{\mathrm{Hx,HF}}[\Phi]|\Phi\rangle, \quad (98)$$

provides the double count correction of the long-range Hartree and exchange energies, in close analogy with the usual MP2 theory. The sum of these two terms provides the total electronic energy in the RSH approximation.

The second-order correction can be formally written as

$$E^{(2)}=-\langle\Phi|\hat{\mathcal{W}}^{\mathrm{lr}}(1+\hat{R}_0\hat{G}^{\overline{\mathrm{sr}}}_0)^{-1}\hat{R}_0\hat{\mathcal{W}}^{\mathrm{lr}}|\Phi\rangle, \quad (99)$$

or, by expanding the inverse operator in Taylor series, as

$$E^{(2)}=-\langle\Phi|\hat{\mathcal{W}}^{\mathrm{lr}}\hat{R}_0\hat{\mathcal{W}}^{\mathrm{lr}}|\Phi\rangle-\sum_{n=1}^{\infty}\langle\Phi|\hat{\mathcal{W}}^{\mathrm{lr}}(-\hat{R}_0\hat{G}^{\overline{\mathrm{sr}}}_0)^n\hat{R}_0\hat{\mathcal{W}}^{\mathrm{lr}}|\Phi\rangle. \quad (100)$$

It is recalled that the short-range screened interaction operator, $\hat{G}^{\overline{\mathrm{sr}}}_0$, takes the form

$$\hat{G}^{\overline{\mathrm{sr}}}_0=2\int\int d\boldsymbol{r}d\boldsymbol{r}'\,\hat{n}(\boldsymbol{r})|\Phi\rangle K^{\overline{\mathrm{sr}}}_{\mathrm{Hxc}}[n_{\Phi}](\boldsymbol{r},\boldsymbol{r}')\langle\Phi|\hat{n}(\boldsymbol{r}'), \quad (101)$$

where the short-range Hartree-exchange-correlation kernel is given by

$$K^{\overline{\mathrm{sr}},\mu}_{\mathrm{Hxc}}[n](\boldsymbol{r},\boldsymbol{r}')=\frac{\delta^2E^{\overline{\mathrm{sr}},\mu}_{\mathrm{Hxc}}[n]}{\delta n(\boldsymbol{r})\,\delta n(\boldsymbol{r}')}. \quad (102)$$

In order to obtain an explicit expression in terms of occupied and virtual RSH orbitals and their eigenvalues, one should insert in Eq. (99) the spectral expansion of the reduced resolvent, Eq. (82), in terms of the excited eigenfunctions Φ_I and eigenvalues $\mathcal{E}_I$ of the effective RSH Hamiltonian. Denoting the contributions to the reduced resolvent coming from single and double excitations by $\hat{R}_0^S$ and $\hat{R}_0^D$, respectively, the analysis of the second-order energy expression can be pursued in terms of matrix elements. It is easy to show that singly excited determinants give vanishing matrix elements with the ground-state determinant, i.e., $\langle\Phi_i^a|\hat{\mathcal{W}}^{\mathrm{lr}}|\Phi\rangle=0$. This is a consequence of a Brillouin-like theorem, which is satisfied by the long-range electron interaction operator,

$$\langle\Phi_i^a|\hat{W}_{ee}^{\mathrm{lr}}|\Phi\rangle = \langle\Phi_i^a|\hat{V}_{\mathrm{H}x,\mathrm{HF}}^{\mathrm{lr}}[\Phi]|\Phi\rangle, \tag{103}$$

as demonstrated in Appendix D. Since only the doubly excited determinants may have nonvanishing contributions and $\hat{V}_{\mathrm{H}x,\mathrm{HF}}^{\mathrm{lr}}[\Phi]$ is a one-electron operator having zero matrix elements between determinants differing in two spin orbitals, the second-order energy correction can be written as

$$E^{(2)} = -\langle\Phi|\hat{W}_{ee}^{\mathrm{lr}}\hat{R}_0^D\hat{W}_{ee}^{\mathrm{lr}}|\Phi\rangle - \sum_{n=1}^{\infty}\langle\Phi|\hat{W}_{ee}^{\mathrm{lr}}(-\hat{R}_0\hat{G}_0^{\overline{\mathrm{sr}}})^n\hat{R}_0^D\hat{W}_{ee}^{\mathrm{lr}}|\Phi\rangle. \tag{104}$$

Furthermore, it should be noted that, as a consequence of the Slater rules, the one-electron charge-density operator, $\hat{n}(\boldsymbol{r})$, has vanishing matrix elements between the determinant Φ and the corresponding doubly excited configurations. Therefore, the double excitations do not enter in the expansion of the screening operator, i.e., $\hat{R}_0^D\hat{G}_0^{\overline{\mathrm{sr}}}=\hat{G}_0^{\overline{\mathrm{sr}}}\hat{R}_0^D=0$, and the second line of Eq. (104), containing nonlinearity contributions, is always zero in the RSH+MP2 framework.

The second-order energy correction is thus reduced to its conventional form,

$$\begin{aligned}E^{(2)} &= -\langle\Phi|\hat{\mathcal{W}}^{\mathrm{lr}}\hat{R}_0^D\hat{\mathcal{W}}^{\mathrm{lr}}|\Phi\rangle\\ &= -\sum_{\substack{i<j\\a<b}}\frac{|\langle\phi_i\phi_j|\hat{w}_{ee}^{\mathrm{lr}}|\phi_a\phi_b\rangle - \langle\phi_i\phi_j|\hat{w}_{ee}^{\mathrm{lr}}|\phi_b\phi_a\rangle|^2}{\varepsilon_a+\varepsilon_b-\varepsilon_i-\varepsilon_j},\end{aligned} \tag{105}$$

where ϕ_r is a spin-orbital of Φ and ε_r is its associated eigenvalue, and $\langle\phi_i\phi_j|\hat{w}_{ee}^{\mathrm{lr}}|\phi_a\phi_b\rangle$ are the two-electron integrals associated with the long-range interaction $w_{ee}^{\mathrm{lr}}(r_{12})$. It should be recalled that the indices i,j refer to occupied spin orbitals and a,b to virtual spin orbitals. Equation (105) is fully analogous to the conventional MP2 energy correction.

From a practical point of view, once the RSH orbitals and one-electron eigenvalues are available, any standard MP2 implementation can be used, provided that the long-range electron repulsion integrals calculated over to the RSH orbitals are used in place of the usual electron repulsion integrals. By virtue of the long-range nature of these integrals, one can take advantage of efficient modern algorithms, like local MP2 [63], multipolar integral approximations, which have particularly favorable convergence properties for the long-range part of the split Coulomb interaction [64], or the resolution of identity approach [65]. It means that in appropriate implementations the extra cost of the MP2 corrections can be made negligible for large systems with respect to the resolution of the self-consistent RSH equations, similar to a usual KS calculations with a hybrid functional. Solid-state applications for semiconductors can also be envisaged in a Wannier orbital-based MP2 implementations [66].

Concerning the MP3 energy expression in a RSH+MPn scheme, one can benefit from the fact that the first-order wave-function correction is entirely due to doubly excited configurations. It means that both the first-order density and potential operator corrections, $n^{(1)}$ and $\hat{\Omega}^{(1)}$, vanish and one can continue to use the traditional MP3 energy expression, as far as the long-range two-electron integral list is used,

$$\begin{aligned}E^{(3)} &= \langle\Phi|\hat{W}_{ee}^{\mathrm{lr}}\hat{R}_0^D\hat{\mathcal{W}}^{\mathrm{lr}}\hat{R}_0^D\hat{W}_{ee}^{\mathrm{lr}}|\Phi\rangle + \langle\Phi|\hat{\mathcal{W}}^{\mathrm{lr}}|\Phi\rangle\\ &\quad\times\langle\Phi|\hat{W}_{ee}^{\mathrm{lr}}\hat{R}_0^D\hat{R}_0^D\hat{W}_{ee}^{\mathrm{lr}}|\Phi\rangle.\end{aligned} \tag{106}$$

The situation is slightly more complicated for the fourth-order correlation energy correction, which involves the second-order wave-function correction. The first-order wave-function correction,

$$|\Phi^{(1)}\rangle = -\hat{R}_0^D\hat{W}_{ee}^{\mathrm{lr}}|\Phi\rangle, \tag{107}$$

contains only double excitations and, as a consequence, the first-order charge-density correction is zero and the second-order wave-function correction obeys the following equation:

$$(1+\hat{R}_0\hat{G}_0^{\overline{\mathrm{sr}}})|\Phi^{(2)}\rangle = \hat{R}_0(\hat{\mathcal{W}}^{\mathrm{lr}} - \langle\hat{\mathcal{W}}^{\mathrm{lr}}\rangle)\hat{R}_0^D\hat{W}_{ee}^{\mathrm{lr}}|\Phi\rangle - \hat{R}_0^S\hat{\Omega}^{(\bar{2})}|\Phi\rangle. \tag{108}$$

Only single excitations contribute to the last term, because the complementary second-order potential, $\hat{\Omega}^{(\bar{2})}$, is a one-electron operator. Writing the second-order wave-function correction in its power series as

$$\begin{aligned}|\Phi^{(2)}\rangle &= \sum_{n=0}^{\infty}(-\hat{R}_0\hat{G}_0^{\mathrm{sr}})^n\hat{R}_0(\hat{\mathcal{W}}^{\mathrm{lr}} - \langle\hat{\mathcal{W}}^{\mathrm{lr}}\rangle)\hat{R}_0^D\hat{W}_{ee}^{\mathrm{lr}}|\Phi\rangle\\ &\quad-\sum_{n=0}^{\infty}(-\hat{R}_0^S\hat{G}_0^{\mathrm{sr}})^n\hat{R}_0^S\hat{\Omega}^{(\bar{2})}|\Phi\rangle,\end{aligned} \tag{109}$$

one can see that the recursion procedure in the second term involves only single excitations. This is not true in the first term, where even higher than double excitations can contribute. Numerical experience would be necessary to evaluate the relative importance of the different kinds of terms at fourth order, but one may hope that nonconventional contributions are negligible.

C. Explicit long-range corrections to the Kohn-Sham equations

An alternative perturbational solution of the range-separated hybrid density-functional problem, defined by the total energy functional, Eq. (90), and the effective Schrödinger equation, Eq. (92), can be sought by choosing a different partitioning scheme for the effective Hamiltonian. As far as one introduces the perturbation operator

$$\hat{\mathfrak{W}}^{\mathrm{lr}} = \hat{W}_{ee}^{\mathrm{lr}} - \hat{V}_{\mathrm{Hxc}}^{\mathrm{lr}}[\Phi^{\mathrm{KS}}], \qquad (110)$$

where the long-range Hartree-exchange-correlation potential $\hat{V}_{\mathrm{Hxc}}^{\mathrm{lr}}[\Phi^{\mathrm{KS}}]$ is chosen such that it sums up with the complementary short-range potential to the total Kohn-Sham potential,

$$\hat{V}_{\mathrm{Hxc}}[\Phi^{\mathrm{KS}}] = \hat{V}_{\mathrm{Hxc}}^{\mathrm{lr}}[\Phi^{\mathrm{KS}}] + \hat{V}_{\mathrm{Hxc}}^{\overline{\mathrm{sr}}}[\Phi^{\mathrm{KS}}], \qquad (111)$$

the zeroth-order problem becomes simply the conventional Kohn-Sham equation. The partitioning in Eq. (110) depends on the range-separation parameter μ, which has been omitted from the equations for the sake of notational simplicity.

While such a scheme has the advantage that the corrections are defined with respect to conventional Kohn-Sham results, one loses definitely the formal simplifications due to the Brillouin-like theorem valid in the previously discussed RSH+MP2 case. The basic equations defining such a model are similar to those described in Sec. IV B. The minimizing wave-function satisfies the effective Schrödinger equation,

$$(\hat{T} + \hat{V}_{ne} + \hat{V}_{\mathrm{Hxc}}^{\mathrm{lr}}[\Phi^{\mathrm{KS}}] + \lambda\hat{\mathfrak{W}}^{\mathrm{lr}} + \hat{V}_{\mathrm{Hxc}}^{\overline{\mathrm{sr}}}[n_\Psi])|\Psi\rangle = \mathcal{E}|\Psi\rangle. \qquad (112)$$

The zeroth-order problem ($\lambda=0$) is just the usual Kohn-Sham one, leading to the Kohn-Sham determinant Φ^{KS}. The following correspondences can be established with the general formulation

$$F[n] = E_{\mathrm{Hxc}}^{\overline{\mathrm{sr}}}[n_\Psi], \qquad (113)$$

$$\hat{\Omega}[n_\Psi] = \hat{V}_{\mathrm{Hxc}}^{\overline{\mathrm{sr}}}[n_\Psi], \qquad (114)$$

$$\hat{W} = \hat{\mathfrak{W}}^{\mathrm{lr}} = \hat{W}_{ee}^{\mathrm{lr}} - \hat{V}_{\mathrm{Hxc}}^{\mathrm{lr}}[\Phi^{\mathrm{KS}}]. \qquad (115)$$

The zeroth-order energy correction,

$$E^{(0)} = \sum_i^{\mathrm{occ}} \varepsilon_i^{\mathrm{KS}} - \langle\Phi^{\mathrm{KS}}|\hat{V}_{\mathrm{Hxc}}^{\overline{\mathrm{sr}}}[n_{\Phi^{\mathrm{KS}}}]|\Phi^{\mathrm{KS}}\rangle + E_{\mathrm{Hxc}}^{\overline{\mathrm{sr}}}[n_{\Phi^{\mathrm{KS}}}], \qquad (116)$$

includes the short-range double count correction, while the first-order energy correction,

$$E^{(1)} = \langle\Phi^{\mathrm{KS}}|\hat{W}_{ee}^{\mathrm{lr}}|\Phi^{\mathrm{KS}}\rangle - \langle\Phi^{\mathrm{KS}}|\hat{V}_{\mathrm{Hxc}}^{\mathrm{lr}}[n_{\Phi^{\mathrm{KS}}}]|\Phi^{\mathrm{KS}}\rangle, \qquad (117)$$

describes the double count correction of the long-range Hartree energy, replaces the density-functional exchange by the Hartree-Fock exchange calculated for the Kohn-Sham determinant, and removes completely the energy associated with the long-range correlation potential. Thus the energy correct up to first order, $E^{[1]}$, is

$$E^{[1]} = \langle\Phi^{\mathrm{KS}}|\hat{T} + \hat{V}_{ne}|\Phi^{\mathrm{KS}}\rangle + E_{\mathrm{H}}[n_{\Phi^{\mathrm{KS}}}] + E_{\mathrm{xc}}^{\overline{\mathrm{sr}}}[n_{\Phi^{\mathrm{KS}}}] + E_x^{\mathrm{lr}}[n_{\Phi^{\mathrm{KS}}}], \qquad (118)$$

where $E_{\mathrm{H}}[n_{\Phi^{\mathrm{KS}}}]$ is the Hartree functional related to the total (long- and short-range) electron interaction.

The second-order energy correction involves matrix elements of the perturbation operator between the Kohn-Sham determinant and singly as well as doubly excited determinants. For singly excited determinants, although the long-range Hartree potential cancels with the matrix element of the long-range *e-e* interaction, there remains a correction due to the difference of the matrix elements of the nonlocal Hartree-Fock exchange and the local DFT exchange-correlation potentials,

$$\langle\Phi_i^a|\hat{W}_{ee}^{\mathrm{lr}} - \hat{V}_{\mathrm{Hxc}}^{\mathrm{lr}}[n_{\Phi^{\mathrm{KS}}}]|\Phi^{\mathrm{KS}}\rangle = -\sum_k^{\mathrm{occ}} \langle\phi_i\phi_k|\phi_k\phi_a\rangle_{\mathrm{lr}} - \langle\phi_i|v_{\mathrm{xc}}^{\mathrm{lr}}|\phi_a\rangle. \qquad (119)$$

As far as the double excitations are concerned, only the matrix elements of the two-electron operator, $\hat{W}_{ee}^{\mathrm{lr}}$, survive.

Starting from Eqs. (66) and (49), and partitioning the reduced resolvent to singly and doubly excited components, $\hat{R}_0=\hat{R}_0^S+\hat{R}_0^D$, the second-order energy correction becomes

$$\begin{aligned} E^{(2)} &= -\sum_{n=0}^{\infty} \langle\Phi|\hat{\mathfrak{W}}^{\mathrm{lr}}(-\hat{R}_0\hat{G}_0^{\overline{\mathrm{sr}}})^n\hat{R}_0\hat{\mathfrak{W}}^{\mathrm{lr}}|\Phi\rangle \\ &= -\sum_{n=0}^{\infty} \langle\Phi|\hat{\mathfrak{W}}^{\mathrm{lr}}(-\hat{R}_0^S\hat{G}_0^{\overline{\mathrm{sr}}})^n(\hat{R}_0^S + \hat{R}_0^D)\hat{\mathfrak{W}}^{\mathrm{lr}}|\Phi\rangle \\ &= -\sum_{n=0}^{\infty} \langle\Phi|\hat{\mathfrak{W}}^{\mathrm{lr}}(-\hat{R}_0^S\hat{G}_0^{\overline{\mathrm{sr}}})^n\hat{R}_0^S\hat{\mathfrak{W}}^{\mathrm{lr}}|\Phi\rangle \\ &\quad - \langle\Phi|\hat{W}_{ee}^{\mathrm{lr}}\hat{R}_0^D\hat{W}_{ee}^{\mathrm{lr}}|\Phi\rangle. \end{aligned} \qquad (120)$$

The interesting point about this result is that the conventional correlation correction calculated from the KS orbitals (last term) is uncoupled from the effects of the relaxation of the KS orbitals due to the removal of the long-range correlation (probably less important) and of the replacement of the long-range DFT exchange by the long-range Hartree-Fock exchange. This alternative partitioning of the problem as compared to the RSH+MP2 scheme is supposed to lead different and probably less good results in comparison with the approach described in Sec. IV B.

V. CONCLUSIONS AND PERSPECTIVES

A general Rayleigh-Schrödinger perturbation theory has been presented for many-electron systems where the total energy is defined as a minimum principle involving a functional of the electron density. An example of outstanding importance is the Kohn-Sham method, or its generalizations including Kohn-Sham-like theories with partially (e.g., long-range) interacting reference systems [11]. As mentioned in the Introduction, other physical situations may lead to mathematically analogous, nonlinear effective Schrödinger equations, such as the reaction-field-type solvent effect models in quantum chemistry [16], or the self-consistent Madelung potential approach [67,68] to handle electrostatic effects in periodic systems. The present RSPT framework allows the treatment of one- and two-electron perturbations. The validity of the $(2n+1)$ rule has been demonstrated in the case of the perturbational expansion of the total energy functional. The wave-function corrections can be obtained self-consistently at each order of the perturbation. Explicit expressions of the term that is responsible for the nonlinearity have been given and shown to be the same for all orders.

In comparison with earlier works, which were either limited to one-electron perturbations applied to an independent-particle system, or the form of the nonlinearity was supposed to take a simple quadratic form, the present work has attempted to provide a unified framework, valid for most of the situations. Such a general perturbation theory was necessary to handle the new type of nonlinearity, raised by the split-Coulomb or range-separated hybrid density-functional methods, which constitute a new and promising way to handle successfully situations in which conventional density functionals seem to fail, i.e., the handling of London dispersion forces, correct evaluation of charge transfer, etc.

As an example of application of the general theory, the coupled Kohn-Sham equations have been rederived for a real one-electron perturbation operator. In addition to this illustration of the approach, MP*n* correlation corrections have been derived for a long-range interacting system, where the short-range electron-electron interactions are taken into account by a density functional. Starting from a self-consistent Hartree-Fock-like independent-particle model of the long-range interactions, the long-range correlation corrections can be developed in a perturbational series, which benefits from a nontrivial cancelation of the nonlinear terms, leading to remarkably simple expressions. The simplicity of the RSH +MP*n* corrections is due to the Hartree-Fock-like partitioning of the Hamiltonian. First applications of this RSH +MP2 theory seem to be very promising to describe van der Waals interactions in a density-functional context [14,15]. Another partition of the problem has been considered too, where the Kohn-Sham independent-particle model serves as zeroth order and the nonlinearity corrections are treated explicitly.

A further development could be the implementation of the higher (third- and fourth-order) Møller-Plesset correlation energy corrections, or application of a double-perturbation approach to treat external one-electron perturbation and electron correlation effects in the mean time. The general formulation makes it possible to envisage other applications as well, such as long-range dynamic correlation corrections on the top of a multideterminental long-range corrected DFT-CI wave function [58].

ACKNOWLEDGMENTS

The author thanks Á. Szabados and I. Mayer for reading the manuscript, and P. R. Surján, A. Savin, J. Toulouse, and E. Fromager for fruitful discussions. Financial support on behalf of the Agence Nationale de la Recherche (ANR) in the framework of the project BLAN06-3143757 is gratefully acknowledged.

APPENDIX A: EXPANSION OF THE FUNCTIONAL AND THE ASSOCIATED POTENTIAL

Using self-explanatory shorthand notations and implicit integration conventions for the repeated lower indices (in fact, coordinates), the lowest-order contributions to the expansion of the density functional are

$$F^{(0)} = F[n^{(0)}], \tag{A1}$$

$$F^{(1)} = \int d\boldsymbol{r} \frac{\delta F}{\delta n(\boldsymbol{r})} n^{(1)}(\boldsymbol{r}) = \omega_{\boldsymbol{r}} n^{(1)}_{\boldsymbol{r}}, \tag{A2}$$

$$F^{(2)} = \frac{1}{2} K^{(2)}_{\boldsymbol{rr}'} n^{(1)}_{\boldsymbol{r}} n^{(1)}_{\boldsymbol{r}'} + \omega_{\boldsymbol{r}} n^{(2)}_{\boldsymbol{r}}, \tag{A3}$$

$$F^{(3)} = \frac{1}{6} K^{(3)}_{\boldsymbol{rr}'\boldsymbol{r}''} n^{(1)}_{\boldsymbol{r}} n^{(1)}_{\boldsymbol{r}'} n^{(1)}_{\boldsymbol{r}''} + K^{(2)}_{\boldsymbol{rr}'} n^{(2)}_{\boldsymbol{r}} n^{(1)}_{\boldsymbol{r}'} + \omega_{\boldsymbol{r}} n^{(3)}_{\boldsymbol{r}}, \tag{A4}$$

$$\begin{aligned} F^{(4)} = {} & \frac{1}{24} K^{(4)}_{\boldsymbol{rr}'\boldsymbol{r}''\boldsymbol{r}'''} n^{(1)}_{\boldsymbol{r}} n^{(1)}_{\boldsymbol{r}'} n^{(1)}_{\boldsymbol{r}''} n^{(1)}_{\boldsymbol{r}'''} \\ & + \frac{1}{2} K^{(3)}_{\boldsymbol{rr}'\boldsymbol{r}''} n^{(2)}_{\boldsymbol{r}} n^{(1)}_{\boldsymbol{r}'} n^{(1)}_{\boldsymbol{r}''} \\ & + \frac{1}{2} K^{(2)}_{\boldsymbol{rr}'} (n^{(2)}_{\boldsymbol{r}} n^{(2)}_{\boldsymbol{r}'} + 2 n^{(1)}_{\boldsymbol{r}} n^{(3)}_{\boldsymbol{r}'}) + \omega_{\boldsymbol{r}} n^{(4)}_{\boldsymbol{r}}. \end{aligned} \tag{A5}$$

The lowest-order terms in the Taylor expansion of the potential are

$$\omega^{(1)}_{\boldsymbol{r}} = K^{(2)}_{\boldsymbol{rr}'} n^{(1)}_{\boldsymbol{r}'}, \tag{A6}$$

$$\omega^{(2)}_{\boldsymbol{r}} = K^{(2)}_{\boldsymbol{rr}'} n^{(2)}_{\boldsymbol{r}'} + \frac{1}{2} K^{(3)}_{\boldsymbol{rr}'\boldsymbol{r}''} n^{(1)}_{\boldsymbol{r}'} n^{(1)}_{\boldsymbol{r}''}, \tag{A7}$$

$$\omega^{(3)}_{\boldsymbol{r}} = K^{(2)}_{\boldsymbol{rr}'} n^{(3)}_{\boldsymbol{r}'} + K^{(3)}_{\boldsymbol{rr}'\boldsymbol{r}''} n^{(1)}_{\boldsymbol{r}'} n^{(2)}_{\boldsymbol{r}''} + \frac{1}{6} K^{(4)}_{\boldsymbol{rr}'\boldsymbol{r}''\boldsymbol{r}'''} n^{(1)}_{\boldsymbol{r}'} n^{(1)}_{\boldsymbol{r}''} n^{(1)}_{\boldsymbol{r}'''}. \tag{A8}$$

APPENDIX B: DERIVATION OF THE THIRD-ORDER ENERGY CORRECTION

Equation (67) still contains the second-order potential operator and the second-order charge density, both violating the $(2n+1)$ rule. By use of the potential operator expansion,

$$\begin{aligned} 2\langle \Psi^{(1)} | \hat{\Omega}^{(2)} | \Psi^{(0)} \rangle &= 2\langle \Psi^{(1)} | \hat{n} | \Psi^{(0)} \rangle \left\{ \frac{\delta^2 F}{\delta n^2} n^{(2)} + \frac{1}{2} \frac{\delta^3 F}{\delta n^3} n^{(1)} n^{(1)} \right\} \\ &= \frac{\delta^2 F}{\delta n^2} n^{(1)} n^{(2)} + \frac{1}{2} \frac{\delta^3 F}{\delta n^3} n^{(1)} n^{(1)} n^{(1)}, \end{aligned} \tag{B1}$$

one obtains

$$E^{(3)} = E_W^{(3)} + E_{\Omega^{(1)}}^{(3)} + \frac{\delta^2 F}{\delta n^2} n^{(1)} n^{(2)} + \frac{1}{2} \frac{\delta^3 F}{\delta n^3} n^{(1)} n^{(1)} n^{(1)} - \frac{1}{3} \frac{\delta^3 F}{\delta n^3} n^{(1)} n^{(1)} n^{(1)} - \frac{\delta^2 F}{\delta n^2} n^{(1)} n^{(2)}, \tag{B2}$$

which leads directly to the final form, Eq. (68), of the third-order energy correction.

APPENDIX C: DERIVATION OF THE FOURTH-ORDER ENERGY CORRECTIONS

After substitution of $\mathcal{E}^{(1)}$ and $\mathcal{E}^{(2)}$ from Eq. (38), and separating $E_W^{(4)}$ and $E_{\Omega^{(1)}}^{(4)}$, one has

$$\begin{aligned} &\langle \Psi^{(1)} | \hat{\Omega}^{(2)} - \langle \hat{\Omega}^{(2)} \rangle | \Psi^{(1)} \rangle + \langle \Psi^{(0)} | \hat{\Omega}^{(2)} | \Psi^{(2)} \rangle \\ &+ 2 \langle \Psi^{(0)} | \hat{\Omega}^{(3)} | \Psi^{(1)} \rangle \\ &- \frac{1}{8} \frac{\delta^4 F}{\delta n^4} n^{(1)} n^{(1)} n^{(1)} n^{(1)} - \frac{\delta^3 F}{\delta n^3} n^{(1)} n^{(1)} n^{(2)} \\ &- \frac{1}{2} \frac{\delta^2 F}{\delta n^2} n^{(2)} n^{(2)} - \frac{\delta^2 F}{\delta n^2} n^{(1)} n^{(3)}. \end{aligned} \tag{C1}$$

Using the definition of the third-order potential, Eq. (A8), one has the relationship

$$2 \langle \Psi^{(0)} | \hat{\Omega}^{(3)} | \Psi^{(1)} \rangle = \frac{1}{6} n^{(1)} \frac{\delta^4 F}{\delta n^4} n^{(1)} n^{(1)} n^{(1)} + n^{(1)} \frac{\delta^3 F}{\delta n^3} n^{(1)} n^{(2)} + n^{(1)} \frac{\delta^2 F}{\delta n^2} n^{(3)} \tag{C2}$$

leading directly to the elimination of the $\delta^3 F / \delta n^3$ and the $\hat{\Omega}^{(3)}$ contributions,

$$\langle \Psi^{(1)} | \hat{\Omega}^{(2)} - \langle \hat{\Omega}^{(2)} \rangle | \Psi^{(1)} \rangle + \langle \Psi^{(0)} | \hat{\Omega}^{(2)} | \Psi^{(2)} \rangle + \frac{1}{24} \frac{\delta^4 F}{\delta n^4} n^{(1)} n^{(1)} n^{(1)} n^{(1)} - \frac{1}{2} \frac{\delta^2 F}{\delta n^2} n^{(2)} n^{(2)}, \tag{C3}$$

free of third-order wave-function corrections. The above two terms are just the contributions identified in the main text as $E_{\Omega^{(2)}}^{(4)}$ and $E_{F^{(2,4)}}^{(4)}$.

APPENDIX D: LONG-RANGE BRILLOUIN THEOREM FOR THE RANGE-SEPARATED HYBRID

Let us calculate the matrix element

$$\langle \Phi_i^a | \hat{W}_{ee}^{\mathrm{lr}} - \hat{V}_{\mathrm{H}x,\mathrm{HF}}^{\mathrm{lr}} | \Phi \rangle. \tag{D1}$$

The matrix element of $\hat{W}_{ee}^{\mathrm{lr}}$ is given by the Slater rules,

$$\langle \Phi_i^a | \hat{W}_{ee}^{\mathrm{lr}} | \Phi \rangle = \sum_k^{\mathrm{occ}} \langle ik | ak \rangle_{\mathrm{lr}} - \langle ik | ka \rangle_{\mathrm{lr}}, \tag{D2}$$

where the summation over the occupied orbitals and the two-electron integrals are defined as

$$\langle ij | kl \rangle_{\mathrm{lr}} = \int \int d\boldsymbol{r} d\boldsymbol{r}' \, \phi_i^*(\boldsymbol{r}) \phi_j^*(\boldsymbol{r}') w_{ee}^{\mathrm{lr}}(\boldsymbol{r},\boldsymbol{r}') \phi_k(\boldsymbol{r}) \phi_l(\boldsymbol{r}). \tag{D3}$$

The long-range Hartree-Fock-potential

$$\langle \Phi_i^a | \hat{V}_{\mathrm{H}x,\mathrm{HF}}^{\mathrm{lr}} | \Phi \rangle = \sum_k \langle ik | ak \rangle_{\mathrm{lr}} - \langle ik | ka \rangle_{\mathrm{lr}}, \tag{D4}$$

which exactly cancels the previous term. The long-range Brillouin theorem follows from the variational character of the range-separated hybrid problem.

---

[1] S. Baroni, S. d. Gironcoli, A. D. Corso, and P. Giannozzi, Rev. Mod. Phys. **73**, 515 (2001).

[2] P. Giannozzi and S. Baroni, "Density functional perturbation theory," in *Handbook of Materials Modeling*, edited by S. Yip (Springer, Berlin, 2005), Vol. XXXIX, pp. 189–208.

[3] S. Baroni, P. Giannozzi, and A. Testa, Phys. Rev. Lett. **58**, 1861 (1987).

[4] X. Gonze and J.-P. Vigneron, Phys. Rev. B **39**, 13120 (1989).

[5] X. Gonze, Phys. Rev. A **52**, 1096 (1995).

[6] X. Gonze, Phys. Rev. A **52**, 1086 (1995).

[7] X. Gonze, P. Ghosez, and R. W. Godby, Phys. Rev. Lett. **74**, 4035 (1995).

[8] X. Gonze, Phys. Rev. B **55**, 10337 (1997).

[9] A. Putrino, D. Sebastiani, and M. Parrinello, J. Chem. Phys. **113**, 7102 (2000).

[10] A. Savin, "On degeneracy, near-degeneracy and density functional theory," in *Recent Developments and Applications of Modern Density Functional Theory*, edited by J. M. Seminario (Elsevier, Amsterdam, 1996), pp. 327–257.

[11] J. Toulouse, F. Colonna, and A. Savin, Phys. Rev. A **70**, 062505 (2004).

[12] J. Paldus, "Perturbation theory," in *Springer Handbook of Atomic, Molecular and Optical Physics*, edited by G. Drake (Springer, New York, 2006).

[13] I. Mayer, *Simple Theorems, Proofs and Derivations in Quantum Chemistry* (Kluwer, New York, 2003).

[14] J. G. Ángyán, I. C. Gerber, A. Savin, and J. Toulouse, Phys. Rev. A **72**, 012510 (2005).

[15] I. C. Gerber and J. G. Ángyán, J. Chem. Phys. **126**, 044103 (2007).

[16] J. G. Ángyán, J. Math. Chem. **10**, 93 (1992).

[17] C. J. Cramer and D. G. Truhlar, Chem. Rev. (Washington, D.C.) **99**, 2161 (1999).

[18] J. Tomasi, B. Mennucci, and R. Cammi, Chem. Rev. (Washington, D.C.) **105**, 2999 (2005).

[19] O. Tapia and O. Goscinski, Mol. Phys. **29**, 1653 (1975).

[20] P. R. Surján and J. G. Ángyán, Phys. Rev. A **28**, 45 (1983).

[21] J. G. Ángyán and P. R. Surján, Phys. Rev. A **44**, 2188 (1991).

[22] J. G. Ángyán, Int. J. Quantum Chem. **47**, 469 (1993).

[23] O. Tapia, E. Poulain, and F. Sussman, Theor. Chim. Acta **47**, 171 (1978).

[24] J. E. Sanhueza, O. Tapia, W. G. Laidlaw, and M. Trsic, J.

Chem. Phys. **70**, 3096 (1979).
[25] E. A. Hylleraas, Z. Phys. **65**, 209 (1930).
[26] E. Wigner, Math. Natur. Anz. (Budapest) **53**, 477 (1935).
[27] A. Dalgarno and A. L. Stewart, Proc. R. Soc. London, Ser. A **238**, 269 (1956).
[28] J. O. Hirschfelder, W. B. Brown, and S. T. Epstein, Adv. Quantum Chem. **1**, 255 (1964).
[29] M. Veithen, X. Gonze, and P. Ghosez, Phys. Rev. B **71**, 125107 (2005).
[30] J. G. Ángyán, Chem. Phys. Lett. **241**, 51 (1995).
[31] R. McWeeny, *Methods of Molecular Quantum Mechanics* (Academic, London, 1989).
[32] A. M. N. Niklasson and M. Challacombe, Phys. Rev. Lett. **92**, 193001 (2004).
[33] J. G. Ángyán, J. Math. Chem. (to be published).
[34] A. Görling and M. Levy, Phys. Rev. B **47**, 13105 (1993).
[35] A. Görling and M. Levy, Phys. Rev. A **50**, 196 (1994).
[36] A. Görling and M. Levy, Int. J. Quantum Chem. **29**, 93 (1995).
[37] C. Filippi, C. J. Umrigar, and X. Gonze, J. Chem. Phys. **107**, 9994 (1997).
[38] S. Ivanov, R. Lopez-Boada, A. Görling, and M. Levy, J. Chem. Phys. **109**, 6280 (1998).
[39] A. Facco Bonetti, E. Engel, R. N. Schmid, and R. M. Dreizler, Phys. Rev. Lett. **86**, 2241 (2001).
[40] S. Ivanov and R. J. Bartlett, J. Chem. Phys. **114**, 1952 (2001).
[41] S. Ivanov and M. Levy, J. Chem. Phys. **116**, 6924 (2002).
[42] I. Grabowski, S. Hirata, S. Ivanov, and R. J. Bartlett, J. Chem. Phys. **116**, 4415 (2002).
[43] S. Ivanov, S. Hirata, I. Grabowski, and R. J. Bartlett, J. Chem. Phys. **118**, 461 (2003).
[44] S. Ivanov and M. Levy, J. Chem. Phys. **119**, 7087 (2003).
[45] R. J. Bartlett, I. Grabowski, S. Hirata, and S. Ivanov, J. Chem. Phys. **122**, 034104 (2005).
[46] R. J. Bartlett, V. F. Lotrich, and I. V. Schweigert, J. Chem. Phys. **123**, 062205 (2005).
[47] H. Jiang and E. Engel, J. Chem. Phys. **123**, 224102 (2005).
[48] E. Engel and H. Jiang, Int. J. Quantum Chem. **106**, 3242 (2006).
[49] M. Levy, Proc. Natl. Acad. Sci. U.S.A. **76**, 6062 (1979).
[50] J. M. Soler, E. Artacho, J. D. Gale, A. García, J. Junquera, P. Ordejón, and D. Sánchez-Portal, J. Phys.: Condens. Matter **14**, 2745 (2002).
[51] R. M. Sternheimer, Phys. Rev. **84**, 244 (1951).
[52] R. M. Sternheimer, Phys. Rev. **96**, 951 (1954).
[53] G. D. Mahan, Phys. Rev. A **22**, 1780 (1980).
[54] F. Dupont-Bourdelet, J. Tillieu, and J. Guy, J. Phys. Radium **21**, 776 (1960).
[55] P. O. Löwdin, J. Math. Phys. **6**, 1341 (1965).
[56] E. Brändas and O. Goscinski, Phys. Rev. A **1**, 552 (1970).
[57] R. Cammi, S. Corni, B. Mennucci, and J. Tomasi, J. Chem. Phys. **122**, 104513 (2005).
[58] E. Fromager and H. J. Aa. Jensen, Phys. Rev. A **78**, 022504 (2008).
[59] H. Stoll and A. Savin, "Density functionals for correlation energies of atoms and molecules," in *Density Functional Methods in Physics*, edited by R. M. Dreizler and J. d. Providencia (Plenum, New York, 1985), pp. 177.
[60] A. Savin, Int. J. Quantum Chem. **S22**, 59 (1988).
[61] J. Toulouse and A. Savin, J. Mol. Struct.: THEOCHEM **762**, 147 (2006).
[62] A. M. Lee, S. W. Taylor, J. P. Dombroski, and P. M. W. Gill, Phys. Rev. A **55**, 3233 (1997).
[63] M. Schütz, G. Hetzer, and H.-J. Werner, J. Chem. Phys. **111**, 5691 (1999).
[64] G. Hetzer, M. Schütz, H. Stoll, and H.-J. Werner, J. Chem. Phys. **113**, 9443 (2000).
[65] M. Sierka, A. Hogekamp, and R. Ahlrichs, J. Chem. Phys. **118**, 9136 (2003).
[66] C. Pisani, M. Busso, G. Capecchi, S. Casassa, R. Dovesi, L. Maschio, C. Zicovich-Wilson, and M. Schütz, J. Chem. Phys. **122**, 094113 (2005).
[67] J. G. Ángyán and B. Silvi, J. Chem. Phys. **86**, 6957 (1987).
[68] G. G. Ferenczy and J. G. Ángyán, J. Comput. Chem. **22**, 1679 (2001).