

Solubility of the optimized-potential-method integral equation for finite systems

E. Engel and H. Jiang

Institut für Theoretische Physik, J. W. Goethe-Universität Frankfurt, Max-von-Laue-Straße 1, D-60438 Frankfurt/Main, Germany

A. Facco Bonetti

Information and Communication Mobile, Siemens AG, Geisenhausener Straße 15, D-81539 München, Germany

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We provide a detailed analysis of the solubility of the optimized-potential-method (OPM) integral equation for the case of the orbital- and eigenvalue-dependent correlation energy functional E_c^{MP2} obtained by second-order perturbation theory on the basis of the Kohn-Sham Hamiltonian. For this functional it was shown [Phys. Rev. Lett., **86**, 2241 (2001)] that for free atoms no solution of the OPM equation can be found which satisfies the boundary condition $v_c^{\text{MP2}}(r \rightarrow \infty) = 0$. On the other hand, there exists a proof that $v_c^{\text{MP2}}(r)$ decays like $1/r^4$ [J. Chem. Phys., **118**, 9504 (2003)]. Here we resolve the obvious contradiction by demonstrating that (i) the OPM equation cannot be solved if continuum states are present, (ii) the OPM equation cannot be solved for a free atom if only a finite number of Rydberg states are included in E_c^{MP2} , and (iii) the OPM equation does allow a solution satisfying $v_c^{\text{MP2}}(r \rightarrow \infty) = 0$ in the case of finite systems with a countable spectrum (exemplified by an atom in a spherical box), if the complete spectrum is taken into account in the OPM procedure.

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I. INTRODUCTION AND SUMMARY OF RESULTS

During recent years the use of implicit density functionals, which depend on the Kohn-Sham (KS) orbitals and eigenvalues rather than just the ground-state density, has developed into a major trend within density functional theory (DFT—for an overview see [1]). The most basic element of this third generation of density functionals for the exchange-correlation (xc) energy E_{xc} is the exact exchange E_x [2–4]. To date, a variety of implementations of the exact E_x are available [5–20], covering the full range of electronic systems of interest.

Unfortunately, applications showed [1,21,22] that the combination of the exact E_x with one of the traditional density functionals for E_c , the local density (LDA) or generalized gradient approximation (GGA), does not yield satisfactory results, as it suffers from a lack of error cancellation between exchange and correlation (which is instrumental for the success of the LDA and GGA). One is thus led to treat correlation on an equal footing as E_x .

However, the orbital-dependent treatment of correlation represents a much more serious challenge than that of exchange. First-principles correlation functionals can be derived on the basis of standard many-body theory, utilizing the KS Hamiltonian as noninteracting reference Hamiltonian [4,22–24]. The most elementary functional of this type is obtained by second-order perturbation theory [24],

$$E_c^{(2)} = E_c^{\text{MP2}} + E_c^{\Delta\text{HF}}, \quad (1)$$

with E_c^{MP2} denoting the second-order Møller-Plesset (MP2) energy correction, formulated with the KS orbitals ϕ_k and KS eigenvalues ϵ_k ,

$$E_c^{\text{MP2}} = \frac{1}{2} \sum_{ijkl} \Theta_i \Theta_j (1 - \Theta_k)(1 - \Theta_l) \times \frac{(ij \parallel kl)[(kl \parallel ij) - (kl \parallel ji)]}{\epsilon_i + \epsilon_j - \epsilon_k - \epsilon_l}, \quad (2)$$

$$(ij \parallel kl) = \int d^3r \int d^3r' \frac{\phi_i^\dagger(\mathbf{r}) \phi_k(\mathbf{r}) \phi_j^\dagger(\mathbf{r}') \phi_l(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \quad (3)$$

and $E_c^{\Delta\text{HF}}$ providing the difference between the exact exchange of DFT and the Hartree-Fock exchange (to lowest order),

$$E_c^{\Delta\text{HF}} = \sum_{il} \frac{\Theta_i(1 - \Theta_l)}{\epsilon_i - \epsilon_l} \left| \langle i | v_x | l \rangle + \sum_j \Theta_j (ij \parallel jl) \right|^2,$$

$$\langle i | v_x | l \rangle = \int d^3r \phi_i^\dagger(\mathbf{r}) v_x(\mathbf{r}) \phi_l(\mathbf{r})$$

($\Theta_i = 1, 0$ indicates whether the KS state i is occupied or not). $E_c^{\Delta\text{HF}}$ is quantitatively much smaller than E_c^{MP2} [22,25] (and quite different in its mathematical structure). Most notably, $E_c^{\Delta\text{HF}}$ vanishes identically for two-electron systems as the helium atom, on which we focus in the present conceptual study. For that reason we will only consider E_c^{MP2} in the rest of this work, while $E_c^{\Delta\text{HF}}$ will be ignored.

The functional (2) is not only the simplest orbital-dependent expression at hand; it also represents the elementary building block of all advanced implicit correlation functionals, both in the case of first-principles extensions [26,27] and in the context of semiempirical approaches [28]. Thus, while E_c^{MP2} cannot be applied to gapless systems (as it is unbounded), it can nevertheless be considered the prototype implicit correlation functional.

The self-consistent application of implicit xc functionals requires the evaluation of the corresponding multiplicative potential v_{xc} via the optimized (effective) potential method (OPM) [5,29]. The core of the OPM is a linear integral equation for v_{xc} , whose source term is provided by the functional derivatives of E_{xc} with respect to the ϕ_i and ϵ_i . The solution of this OPM equation turns out to be straightforward, though computationally demanding, in the case of the exact E_x .

On the other hand, an attempt to calculate the potential v_c^{MP2} resulting from E_c^{MP2} for free atoms failed [30] (in the following referred to as I). In I this failure was shown to be related to the behavior of the ingredients of the OPM integral equation for large r , which, in turn, led to the conclusion that v_c^{MP2} diverges asymptotically. This result has later been challenged by Niquet, Fuchs, and Gonze (NFG) in a series of papers [31–33]. Within the framework of the adiabatic connection NFG show that for finite systems v_c^{MP2} should decay like $-\alpha/(2r^4)$, just as the exact v_c [4,34]. As some of the arguments in I are of numerical nature, NFG relate the contradiction between the conclusion of I and their own results to numerical inadequacies. In response to NFG additional information on the handling of E_c^{MP2} in I has been provided in Ref. [35]. In particular, it has been shown analytically that any MP2-type functional depending on a finite number of unoccupied Rydberg states will lead to an asymptotically diverging potential.

It is obvious that the solubility of the OPM equation questioned in I is of central importance for further development of orbital-dependent correlation functionals. In this contribution this question is settled by a detailed analysis of the OPM equation for spherical, spin-saturated systems, using atomic helium as explicit example, wherever necessary. In fact, it will be shown that the results of both I and NFG are correct, if restricted to their respective regimes of validity. Moreover, while many of our results will be explicitly derived on the basis of E_c^{MP2} , we believe that the conclusions emerging from this analysis are valid beyond this specific functional. Similarly, there can be little doubt that our results apply quite generally to all finite systems.

As already pointed out in Ref. [35] the continuum states play a crucial role for the solubility of the OPM equation in the case of a free atom. On the basis of the standard treatment of the positive energy continuum, which is briefly reviewed in Sec. II, we demonstrate in Secs. III and IV that the OPM equation does not allow a solution if the energy functional depends on the continuum states. The proof proceeds by *reductio ad absurdum*: Assuming the potential $v_c^{\text{MP2}}(r)$ to vanish in the limit $r \rightarrow \infty$, the resulting presence of the positive energy continuum leads to a violation of a crucial sum rule which must be satisfied by the OPM equation in order to be soluble. One thus concludes that v_c^{MP2} cannot approach zero for large r , but rather diverges, in this way suppressing the positive energy continuum.

In Sec. V we then consider the asymptotic behavior of the various ingredients of the OPM equation for free atoms. It is shown, analytically, that for any functional which depends on a finite number of unoccupied Rydberg states only no solution with $v_c(r \rightarrow \infty) = 0$ exists. For the case of E_c^{MP2} we demonstrate numerically that a resummation of all Rydberg contributions does not resolve this problem. In addition, we consider the solution of the OPM equation within a finite Hilbert space, spanned by a number of KS Rydberg states. Assuming $v_c(r \rightarrow \infty) = 0$, an analysis of the asymptotic decay of the left-hand and right-hand sides of the OPM equation leads to a contradiction, so that again no solution can be found which is consistent with $v_c(r \rightarrow \infty) = 0$. While the rigorous mathematical contradiction is resolved as soon as the

finite Hilbert space is defined by a number of basis functions (rather than exact KS states), the resulting potential is nevertheless expected to show some remnants of the divergence.

In order to demonstrate the consistency of these results with NFG, we consider an atom in a spherical cavity, requiring hard-wall boundary conditions (in Sec. VI). For this system with a countable spectrum and compact support we verify numerically the desired solubility of the OPM equation. It is shown, in particular, that completeness of all sums-over-states involved is important to obtain a regular asymptotic behavior of the OPM equation. Lack of completeness (in the Hilbert space defined by the KS Hamiltonian plus boundary conditions) is the reason why for free atoms even the inclusion of the full Rydberg series in E_c^{MP2} does not allow a solution with $v_c^{\text{MP2}}(r \rightarrow \infty) = 0$.

Finally, in Sec. VII we investigate the transition from the atom in a box to the free atom in detail, in order to pinpoint the origin of the divergence observed for the latter. The problem is traced to an order of limits ambiguity: The OPM equation cannot be solved after the continuum limit has been taken. Any practical realization thus has to ensure a countable spectrum by suitable boundary conditions, even if ultimately the limit of a free system is of interest.

At this point quite naturally the question arises as to whether these difficulties are related to the unboundedness of E_c^{MP2} . In order to answer this question it has to be emphasized that for all steps of the present analysis a given, fixed KS spectrum with a nonzero highest occupied and lowest unoccupied molecular orbital (HOMO-LUMO) gap is utilized; i.e., we address the solubility of the OPM equation within a single cycle of the KS iteration towards self-consistency. In other words, in the present work the OPM is not applied in the sense of a complete energy-minimization procedure which could gain energy by closing the HOMO-LUMO gap, but rather as a tool for evaluating $\delta E_c^{\text{MP2}} / \delta n$ for given KS orbitals and eigenvalues. None of our arguments relies on the specific form of the eigenvalue denominator of E_c^{MP2} ; only the symmetry of this functional with respect to the possible virtual excitations is exploited. In fact, if one artificially introduces some state-independent constant energy separation between occupied and unoccupied states in the eigenvalue denominator (so that the resulting functional is bounded), none of our conclusions is affected. Moreover, as already pointed out, many conclusions are valid quite generally for all kinds of functionals which depend on the unoccupied KS states. This is true in particular for the violation of the crucial OPM sum rule for systems with a positive-energy continuum: This violation results from the unsymmetric treatment of discrete and continuum energies in the OPM, but not from the form of E_c^{MP2} . On the other hand, the discretization of the spectrum by boundary conditions, which restores the solubility, does in no way ensure a nonzero HOMO-LUMO gap. For these reasons there can be no doubt that the problems with the solubility of the OPM equation addressed in this contribution are not intrinsically related to the unboundedness of E_c^{MP2} .

It is a second question whether a nonzero HOMO-LUMO gap can survive a self-consistent application of E_c^{MP2} . In this respect, it seems worthwhile to point out that we have performed self-consistent calculations for the helium atom in a

cavity without experiencing a breakdown of the gap [36]. It remains to be examined whether the same is true for more critical systems like the beryllium atom or the dissociation limit of molecules like N_2 . Not only for these systems, but rather quite generally it seems physically more appropriate to resort to a resummed form of the KS perturbation series like the random phase approximation (RPA) [26,27], which does not suffer from unboundedness. It is obvious that E_c^{MP2} can only serve as a starting point for the discussion of implicit correlation functionals.

The units $\hbar=e^2=1$ will be used throughout this paper.

II. CONTINUUM STATES: BASICS

In this section we briefly review the basic properties of the positive-energy solutions of the KS equations for free atoms, in order to introduce our notation and to set the stage for a discussion of their role in the OPM integral equation. For spherical, spin-saturated, closed-subshell systems all KS states can be written as

$$\phi_{nlm}(\mathbf{r}) = \frac{P_{nl}(r)}{r} Y_{lm}(\Omega), \quad (4)$$

where n at this point may denote a continuous quantum number and Y_{lm} represents the standard spherical harmonics. The radial orbitals P_{nl} satisfy the radial KS equations

$$\{\hat{T}_l + v_s(r) - \epsilon_{nl}\}P_{nl}(r) = 0, \quad (5)$$

with the kinetic energy operator being abbreviated by \hat{T}_l ,

$$\hat{T}_l = \frac{-1}{2m} \left[\frac{\partial^2}{\partial r^2} - \frac{l(l+1)}{r^2} \right]. \quad (6)$$

The P_{nl} can be chosen to be real, and we will follow this standard throughout this work.

If the potential $v_s(r)$ vanishes in the limit $r \rightarrow \infty$,

$$v_s(r \rightarrow \infty) \sim -\frac{Z}{r} \quad (Z \geq 0) \quad (7)$$

[precisely, if $v_s(r)$ approaches a constant which is then chosen as the zero of the energy scale], the differential equation (5) can be solved for any real, positive ϵ_{nl} , so that for each l a continuum of positive-energy solutions exists. The positive-energy continuum states are most conveniently classified by the momentum

$$k = (2m\epsilon)^{1/2}, \quad (8)$$

rather than the energy ϵ itself,

$$\left\{ \hat{T}_l + v_s(r) - \frac{k^2}{2m} \right\} \bar{P}_{kl}(r) = 0, \quad (9)$$

and normalized as

$$\bar{P}_{kl}(r \rightarrow \infty) \sim \sqrt{\frac{2}{\pi}} \sin \left[kr + \frac{Zm}{k} \ln(2kr) - \frac{\pi}{2}l - \eta_{kl} \right]. \quad (10)$$

The Coulomb phase $(Zm/k)\ln(2kr)$ and η_{kl} provide the phase shift by which the solutions of Eq. (9) differ from those of

the free radial Schrödinger equation due to the presence of $v_s(r)$. η_{kl} is obtained by outward integration of \bar{P}_{kl} , starting with the boundary condition $\bar{P}_{kl}(r=0)=0$ and a corresponding condition for $\partial \bar{P}_{kl}/\partial r$ consistent with the form of $v_s(r=0)$ (i.e., the cusp condition for point nuclei). The normalization (10) implies a linear scaling of the norm inside a (large) sphere with the radius R of the sphere,

$$\int_0^R dr \bar{P}_{kl}(r)^2 = \frac{R}{\pi} + \dots \quad (11)$$

All corrections to Eq. (11) due to the deviation of \bar{P}_{kl} from its asymptotic form (10), etc., are small compared to the leading term (see Appendix A). States with the normalization (11) will be denoted by \bar{P}_{kl} in the following.

With the normalization (11) the orthonormality relation of the continuum states has a particularly simple form

$$\int_0^\infty dr \bar{P}_{kl}(r) \bar{P}_{k'l}(r) = \delta(k-k'). \quad (12)$$

In addition, all positive-energy states are orthogonal to the discrete, negative-energy states P_{nl} ,

$$\int_0^\infty dr P_{nl}(r) \bar{P}_{kl}(r) = 0, \quad (13)$$

which are always chosen to be normalized to 1,

$$\int_0^\infty dr P_{nl}(r) P_{n'l}(r) = \delta_{nn'}. \quad (14)$$

Together with the countable set of negative-energy eigenstates, the continuum states \bar{P}_{kl} constitute the Hilbert space emerging from the KS Hamiltonian plus the free-atom boundary conditions (more precisely, they constitute the dual space corresponding to the Hamiltonian and its domain—we will, however, not distinguish between these spaces in the following, but always refer to this space as Hilbert space). The completeness relation in this Hilbert space is given by

$$\sum_n P_{nl}(r) P_{nl}(r') + \int_0^\infty dk \bar{P}_{kl}(r) \bar{P}_{kl}(r') = \delta(r-r'), \quad (15)$$

with the sum over n going through all discrete levels.

III. CONTINUUM STATES: CONSEQUENCES FOR THE OPM PROCEDURE

Let us now consider the consequences of the presence of continuum states for the various ingredients of the OPM integral equation. The radial OPM equation relevant for spherical, closed-subshell systems is most easily derived by use of the chain rule for functional differentiation. For any functional E_{xc} of the radial orbitals and eigenvalues the functional derivative with respect to the spherical KS potential $v_s(r)$ can be expressed by its functional derivative with respect to the radial density $4\pi r^2 n(r)$ by use of the unique correspondence between n and v_s ,

$$\int_0^\infty dr' K(r, r') v_{xc}(r') = \frac{\delta E_{xc}}{\delta v_s(r)} =: Q_{xc}(r), \quad (16)$$

where K denotes the radial response function,

$$K(r, r') = \frac{\delta[4\pi r'^2 n(r')]}{\delta v_s(r)}, \quad (17)$$

and v_{xc} is the spherical potential corresponding to E_{xc} ,

$$v_{xc}(r) = \frac{\delta E_{xc}}{\delta n(r)}. \quad (18)$$

Using the radial density,

$$4\pi r^2 n(r) = 2 \sum_{nl} \Theta_{nl}(2l+1) P_{nl}(r)^2, \quad (19)$$

$$\Theta_{nl} = \begin{cases} 1 & \text{for } \epsilon_{nl} \leq \epsilon_F, \\ 0 & \text{otherwise,} \end{cases} \quad (20)$$

the kernel K can be written as

$$K(r, r') = -4 \sum_{nl} \Theta_{nl}(2l+1) P_{nl}(r) G_{nl}(r, r') P_{nl}(r'), \quad (21)$$

with the Green's function

$$G_{nl}(r, r') = \sum_{n'l' \neq n} \frac{P_{n'l'}(r) P_{n'l'}(r')}{\epsilon_{n'l'} - \epsilon_{nl}} + \int_0^\infty dk \frac{\bar{P}_{kl}(r) \bar{P}_{kl}(r')}{\epsilon - \epsilon_{nl}}. \quad (22)$$

In Eq. (22) the integral over all positive-energy continuum states accounts for the completeness relation (15) of the present Hilbert space. A derivation of Eq. (21) is given in Appendix B. Here we only note that G_{nl} satisfies the differential equation

$$\{\hat{T}_l + v_s(r) - \epsilon_{nl}\} G_{nl}(r, r') = \delta(r - r') - P_{nl}(r) P_{nl}(r'), \quad (23)$$

with the boundary condition

$$\int_0^\infty dr' G_{nl}(r, r') P_{nl}(r') = \int_0^\infty dr P_{nl}(r) G_{nl}(r, r') = 0. \quad (24)$$

Both Eqs. (23) and (24) can be verified by direct insertion of Eq. (22) and use of Eqs. (13)–(15).

The right-hand side of Eq. (16) can be evaluated for any given functional E_{xc} , once the functional derivative with respect to v_s is replaced by a derivative with respect to the actual ingredients of E_{xc} . Relying on the results of Appendix B one finds

$$Q_{xc}(r) = Q_{xc,-}^a(r) + Q_{xc,+}^a(r) + Q_{xc}^b(r), \quad (25)$$

$$Q_{xc,-}^a(r) = - \sum_{nl} \int_0^\infty dr' P_{nl}(r) G_{nl}(r, r') \frac{\delta E_{xc}}{\delta P_{nl}(r')}, \quad (26)$$

$$Q_{xc,+}^a(r) = - \sum_l \int_0^\infty dk \int_0^\infty dr' \bar{P}_{kl}(r) G_{kl}(r, r') \frac{\delta E_{xc}}{\delta \bar{P}_{kl}(r')}, \quad (27)$$

$$Q_{xc}^b(r) = \sum_{nl} P_{nl}(r)^2 \frac{\delta E_{xc}}{\delta \epsilon_{nl}}, \quad (28)$$

with the Green's function

$$G_{kl}(r, r') = \sum_{n'} \frac{P_{n'l}(r) P_{n'l}(r')}{\epsilon_{n'l} - \epsilon} + \mathcal{P} \int_0^\infty dk' \frac{\bar{P}_{k'l}(r) \bar{P}_{k'l}(r')}{\epsilon' - \epsilon} \quad (29)$$

for the positive-energy states. In analogy to Eqs. (23) and (24), G_{kl} satisfies the differential equation

$$\left\{ \hat{T}_l + v_s(r) - \frac{k^2}{2m} \right\} G_{kl}(r, r') = \delta(r - r') \quad (30)$$

and has the projection property

$$\int_0^\infty dr' G_{kl}(r, r') \bar{P}_{kl}(r') = \int_0^\infty dr \bar{P}_{kl}(r) G_{kl}(r, r') = 0, \quad (31)$$

with the principal value of the k' integral in Eq. (29) being instrumental for Eq. (31). Note that in contrast to the restricted sum over nl in Eq. (21) the sums-over-states in Eqs. (26) and (27) comprise all unoccupied states, including the positive continuum. On the other hand, the sum-over-states in the eigenvalue derivative term (28) is restricted to the discrete levels: As long as v_s vanishes for $r \rightarrow \infty$, one can always find a solution of Eq. (9) for any given energy ϵ , irrespectively of the detailed form of v_s .

Up to this point all relations are valid for arbitrary functionals E_{xc} of the states and eigenvalues. For a complete analysis one needs the explicit form of E_{xc} . In this contribution we focus on the second-order perturbative functional E_c^{MP2} . The corresponding expression including continuum states was first given by Kelly [37]. It can be decomposed into three components,

$$E_c^{\text{MP2}} = E_c^{\text{DD}} + 2E_c^{\text{DC}} + E_c^{\text{CC}}, \quad (32)$$

according to the possible virtual excitation of two KS particles from occupied discrete levels into two unoccupied discrete states,

$$E_c^{\text{DD}} = \sum_{\substack{n_1 n_2 n_3 n_4 \\ l_1 l_2 l_3 l_4}} \frac{N(n_1 l_1, n_2 l_2 | n_3 l_3, n_4 l_4)}{\epsilon_{n_1 l_1} + \epsilon_{n_2 l_2} - \epsilon_{n_3 l_3} - \epsilon_{n_4 l_4}}, \quad (33)$$

one discrete and one continuum state,

$$E_c^{\text{DC}} = \sum_{n_1 n_2 n_3} \int_0^\infty dk \sum_l \frac{N(n_1 l_1, n_2 l_2 | n_3 l_3, \bar{k} l)}{\epsilon_{n_1 l_1} + \epsilon_{n_2 l_2} - \epsilon_{n_3 l_3} - \epsilon}, \quad (34)$$

or two continuum states,

$$E_c^{\text{CC}} = \sum_{n_1 n_2} \int_0^\infty dk \int_0^\infty dk' \sum_{l l'} \frac{N(n_1 l_1, n_2 l_2 | \bar{k} l, \bar{k}' l')}{\epsilon_{n_1 l_1} + \epsilon_{n_2 l_2} - \epsilon - \epsilon'}. \quad (35)$$

In Eqs. (33)–(35), N abbreviates the appropriate product of occupation factors, angular momentum coupling coefficients, and radial Slater integrals,

$$N(12|34) = \Theta_1 \Theta_2 (1 - \Theta_3)(1 - \Theta_4) [D(12|34) - X(12|34)], \quad (36)$$

$$D(12|34) = 2 \sum_{L=0}^{\infty} (12|34)_L^2 (l_1 0 l_3 0 | L 0)^2 (l_2 0 l_4 0 | L 0)^2 \times \frac{(2l_1 + 1)(2l_2 + 1)(2l_3 + 1)(2l_4 + 1)}{(2L + 1)^3}, \quad (37)$$

$$X(12|34) = \sum_{L, L'=0}^{\infty} (-1)^{l_1 + l_2 + l_3 + l_4 + L + L'} \times (12|34)_L (12|43)_{L'} W(l_1 l_3 l_4 l_2; LL') (l_1 0 l_3 0 | L 0) \times (l_2 0 l_4 0 | L 0) (l_1 0 l_4 0 | L' 0) (l_2 0 l_3 0 | L' 0) \times \frac{(2l_1 + 1)(2l_2 + 1)(2l_3 + 1)(2l_4 + 1)}{(2L + 1)(2L' + 1)}, \quad (38)$$

where $(l_1 m_1 l_2 m_2 | LM)$ denotes a Clebsch-Gordan coefficient, $W(l_1 l_3 l_4 l_2; LL')$ denotes a Racah coefficient (both in the definition of Rose [38]), and the radial Slater integral is given by

$$(12|34)_L = \int_0^{\infty} dr \int_0^{\infty} dr' \frac{r^L}{r'^{L+1}} P_1(r) P_3(r) P_2(r') P_4(r'). \quad (39)$$

The overbars in $N(n_1 l_1, n_2 l_2 | \overline{kl}, \overline{k'l'})$ indicate that the third and fourth orbitals to be used in the corresponding Slater integrals (39) are continuum states with the normalization (11). For later reference we also list the form of N for the case of helium-like systems with $n_1 = n_2 = 1$, $l_1 = l_2 = 0$,

$$[D(12|34) - X(12|34)]^{\text{He}} = \delta_{l_3 l_4} \frac{(12|34)_l^2}{2l_3 + 1}. \quad (40)$$

IV. SOLUBILITY OF OPM EQUATION FOR SYSTEMS WITH CONTINUUM STATES

With the relations collected in Sec. III it is now straightforward to analyze the solubility of the OPM equation for systems with a positive-energy continuum. The first point to be noted is the fact that Eq. (24) ensures that the integral over the left-hand side of Eq. (16) exists and vanishes,

$$\int_0^{\infty} dr \int_0^{\infty} dr' K(r, r') v_{xc}(r') = 0 \quad (41)$$

(provided that the r integration can be interchanged with the r' integration). An analogous relation is found for the a -contribution to the inhomogeneity,

$$\int_0^{\infty} dr Q_{xc,-}^a(r) = \int_0^{\infty} dr Q_{xc,+}^a(r) = 0, \quad (42)$$

where, in addition to Eq. (24), Eq. (31) has been utilized. However, the same is not true for Q_{xc}^b . In the case of the MP2 functional use of Eq. (14) gives

$$\int_0^{\infty} dr Q_c^b(r) = \sum_{nl} \left[\frac{\partial E_c^{\text{DD}}}{\partial \epsilon_{nl}} + 2 \frac{\partial E_c^{\text{DC}}}{\partial \epsilon_{nl}} + \frac{\partial E_c^{\text{CC}}}{\partial \epsilon_{nl}} \right]. \quad (43)$$

Inspection of Eq. (33) shows that

$$\sum_{nl} \frac{\partial E_c^{\text{DD}}}{\partial \epsilon_{nl}} = 0, \quad (44)$$

due to the symmetry of E_c^{DD} . On the other hand, the remaining terms

$$\sum_{nl} \frac{\partial E_c^{\text{DC}}}{\partial \epsilon_{nl}} = - \sum_{\substack{n_1 n_2 n_3 \\ l_1 l_2 l_3}} \int_0^{\infty} dk \sum_l \frac{N(n_1 l_1, n_2 l_2 | n_3 l_3, \overline{kl})}{(\epsilon_{n_1 l_1} + \epsilon_{n_2 l_2} - \epsilon_{n_3 l_3} - \epsilon)^2}, \quad (45)$$

$$\sum_{nl} \frac{\partial E_c^{\text{CC}}}{\partial \epsilon_{nl}} = -2 \sum_{\substack{n_1 n_2 \\ l_1 l_2}} \int_0^{\infty} dk \int_0^{\infty} dk' \sum_{l'l'} \frac{N(n_1 l_1, n_2 l_2 | \overline{kl}, \overline{k'l'})}{(\epsilon_{n_1 l_1} + \epsilon_{n_2 l_2} - \epsilon - \epsilon')^2} \quad (46)$$

do not vanish, as the presence of the continuum states breaks the symmetry of these energy contributions. By insertion of the special case of helium, Eqs. (36) and (40), one can explicitly verify that the individual terms in Eqs. (45) and (46) cannot cancel each other, as both the numerators and the eigenvalue denominators are strictly positive. One thus ends up with

$$\int_0^{\infty} dr Q_c^b(r) \neq 0, \quad (47)$$

in obvious contradiction to Eqs. (41), (42), and (16). One thus concludes that the OPM equation (16) does not allow a solution for total potentials v_s which vanish in the limit $r \rightarrow \infty$, as this latter property automatically implies the existence of positive-energy continuum states.

V. SOLUBILITY OF OPM EQUATION: RYDBERG STATES ONLY

Let us now examine the OPM equation (16) in the asymptotic regime of large r , again under the assumption that the total potential v_s vanishes in the limit $r \rightarrow \infty$. In order to provide the basis for this analysis we first express the Green's function G_{nl} for discrete levels in terms of the second, non-normalizable solution S_{nl} of the KS equation for the eigenvalue ϵ_{nl} ,

$$\{\hat{T}_l + v_s(r) - \epsilon_{nl}\} S_{nl}(r) = 0. \quad (48)$$

If one chooses the normalization of S_{nl} so that

$$P_{nl}(r) S'_{nl}(r) - P'_{nl}(r) S_{nl}(r) = 1, \quad (49)$$

one can show by direct insertion that

$$G_{nl}(r, r') = 2m \left\{ \Theta(r - r') P_{nl}(r) S_{nl}(r') + \Theta(r' - r) S_{nl}(r) P_{nl}(r') - P_{nl}(r) \left[P_{nl}(r') \int_0^{r'} dx P_{nl}(x) S_{nl}(x) + S_{nl}(r') \int_{r'}^{\infty} dx P_{nl}(x)^2 \right] \right. \\ \left. - P_{nl}(r') \left[P_{nl}(r) \int_0^r dx P_{nl}(x) S_{nl}(x) + S_{nl}(r) \int_r^{\infty} dx P_{nl}(x)^2 \right] + 2 P_{nl}(r) P_{nl}(r') \int_0^{\infty} dx \int_0^x dy P_{nl}(x)^2 P_{nl}(y) S_{nl}(y) \right\} \quad (50)$$

satisfies both the differential equation (23) and the constraining boundary condition (24). The exact representation (50) of G_{nl} is much easier to handle than the original sum-over-states form (22), both analytically and numerically [5].

In addition, Eq. (50) is an ideal tool to demonstrate the importance of the continuum states in Eq. (22). In Fig. 1 two forms of the Green's function for the $1s$ orbital of the helium ground state are shown: The exact representation (52) is compared with the Rydberg contribution to Eq. (22), including differently many shells. It is obvious that for any given r the sum over the Rydberg states converges rapidly, the contribution of higher-lying Rydberg states being relevant only in the asymptotic regime. On the other hand, the converged result for finite r is still quite far from the complete G_{1s} , thus emphasizing the large contribution of the continuum states to Eq. (22).

Equation (50) is also the ideal starting point for an analysis of the asymptotic behavior of the left-hand side of Eq. (16). If for large r the total potential vanishes according to Eq. (7), the discrete KS orbitals decay as

$$P_{nl}(r \rightarrow \infty) \sim A_{nl} r^{\beta_{nl}} e^{-\alpha_{nl} r} \quad (51)$$

($\alpha_{nl} = \sqrt{-2\epsilon_{nl}}$, $\beta_{nl} = Z/\alpha_{nl}$). It is then straightforward to extract the asymptotic behavior of the S_{nl} from Eqs. (48) and (49),

$$S_{nl}(r \rightarrow \infty) \sim \frac{1}{2\alpha_{nl} A_{nl}} r^{-\beta_{nl}} e^{\alpha_{nl} r}. \quad (52)$$

Of course, Eq. (7) implies that the xc potential decays accordingly. Let us therefore assume that the solution v_{xc} of Eq. (16) behaves as

$$v_{xc}(r \rightarrow \infty) \sim -\frac{Z_{xc}}{r}, \quad (53)$$

which includes the case of the exact exchange, for which $Z_x = 1$. The correlation potential, on the other hand, will be assumed to vanish at least as fast as r^{-2} —i.e., $Z'_c = 0$. In fact, the correlation component is expected to decay as r^{-4} . Combining both solutions (51) and (52) with the assumption, Eq. (53), one finds, for $r \rightarrow \infty$,

$$P_{nl}(r) S_{nl}(r) \sim \frac{1}{2\alpha_{nl}}, \quad (54)$$

$$\int_r^{\infty} dx P_{nl}(x)^2 \sim \frac{1}{2\alpha_{nl}} P_{nl}(r)^2, \quad (55)$$

$$\int_r^{\infty} dx P_{nl}(x)^2 v_{xc}(x) \sim \frac{1}{2\alpha_{nl}} P_{nl}(r)^2 v_{xc}(r), \quad (56)$$

$$\int_0^r dx P_{nl}(x) S_{nl}(x) \sim \frac{1}{2\alpha_{nl}} r, \quad (57)$$

$$\int_0^r dx P_{nl}(x) S_{nl}(x) v_{xc}(x) \sim \frac{-Z_{xc}}{2\alpha_{nl}} \ln(r). \quad (58)$$

With these relations it is straightforward to identify the asymptotically leading contribution to the left-hand side of Eq. (16) by insertion of Eq. (50),

$$\int_0^{\infty} dr' K(r, r') v_{xc}(r') \sim 8m(2I_F + 1) P_F(r)^2 \int_0^r dx P_F(x) S_F(x) \\ \times \int_0^{\infty} dr' P_F(r')^2 v_{xc}(r'), \quad (59)$$

where the index F characterizes the highest occupied KS state.

This result implies that the asymptotic decay of the left-hand side of Eq. (16) is independent of the potential considered; v_{xc} only enters via its expectation value. In particular, one finds that the inhomogeneity Q_c for any correlation functional vanishes just as the inhomogeneity Q_x for the exact exchange [30],

$$\frac{Q_c(r)}{Q_x(r)} = \frac{\int_0^{\infty} dr' K(r, r') v_c(r')}{\int_0^{\infty} dr' K(r, r') v_x(r')} \xrightarrow{r \rightarrow \infty} \frac{\int_0^{\infty} dx P_F(x)^2 v_c(x)}{\int_0^{\infty} dy P_F(y)^2 v_x(y)} = \text{const.} \quad (60)$$

Let us now examine the asymptotic behavior of Q_c for the case of the MP2 functional in some detail. If one restricts the functional to excitations into a finite number of Rydberg states, one finds, by insertion of Eqs. (50) and (33) into Eq. (26) and use of Eqs. (54)–(58),

$$Q_c^a(r) \sim \frac{m}{\alpha_M} r P_M(r)^2 \int_0^{\infty} dx P_M(x) \frac{\delta E_c^{\text{DD}}}{\delta P_M(x)}, \quad (61)$$

where M characterizes the highest unoccupied Rydberg level included in E_c^{DD} . An analogous analysis of Q_c^b leads to

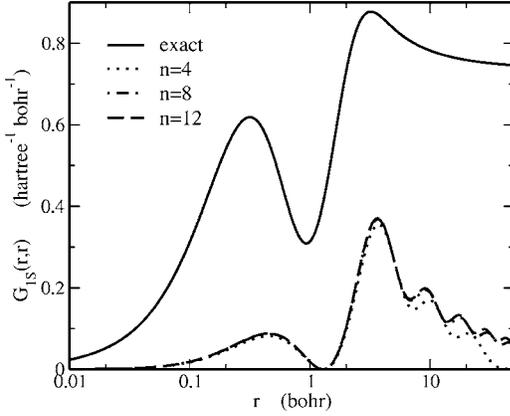


FIG. 1. $G_{1s}(r,r)$ for the He atom: exact result (50) versus sum-over-states form (22), in which only a finite number of unoccupied Rydberg shells is included.

$$Q_c^b(r) \sim P_M(r)^2 \frac{\partial E_c^{DD}}{\partial \epsilon_M}. \quad (62)$$

It is immediately clear that (i) the decay observed in Eq. (59) is completely different from that in Eqs. (61) and (62) and that (ii) Q_c^a and Q_c^b do not cancel asymptotically. One thus concludes that no asymptotically vanishing solution of the OPM equation exists, as long as the energy functional depends on a finite number of Rydberg states only. Moreover, the detailed form of E_c^{DD} is irrelevant for the present argument, which only relies on $\delta E_c / \delta P_M(x) \neq 0$ and $\partial E_c / \partial \epsilon_M \neq 0$. Consequently, the conclusion applies quite generally.

What happens if one tries to include the complete Rydberg series in E_c^{DD} ? The answer can no longer be given analytically. In Fig. 2 we thus show the dependence of Q_c on M (all quantities in Figs. 2 and 3 have been evaluated from self-consistent x-only solutions, obtained fully numerically by finite differences methods on a radial mesh of 6400 points—the differences resulting from use of the exact KS states [39] rather than the x-only states are not visible in the plots). For any given r -value Q_c shows a clear convergence with increasing M . Figure 2 also exhibits the oscillatory na-

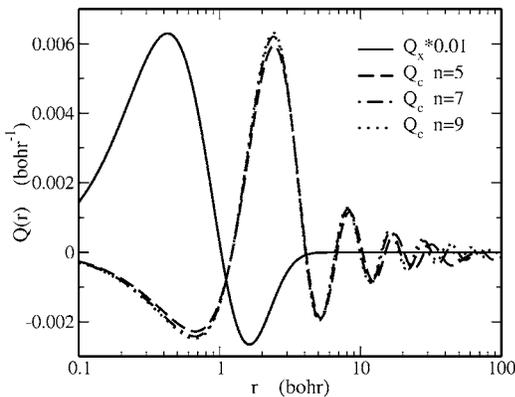


FIG. 2. Q_c for the He atom: dependence of Q_c on the number of unoccupied Rydberg states included in E_c^{DD} . For comparison also Q_x is plotted.

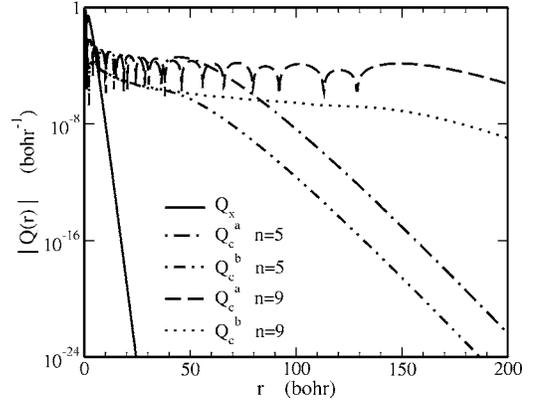


FIG. 3. Absolute value of Q_c for the He atom: dependence of individual components on the number of unoccupied Rydberg states included in E_c^{DD} . For comparison also Q_x is plotted.

ture of Q_c , consistent with $\sum_{nl} \partial E_c^{DD} / \partial \epsilon_{nl} = 0$. On the other hand, Q_c decays much more slowly than Q_x . This latter point becomes even more obvious in Fig. 3, in which the absolute values of Q_c^a and Q_c^b are compared to that of Q_x on a logarithmic scale. One observes a dramatic difference between the decay of Q_x and that of the components of Q_c . Both components decay more and more slowly with increasing M . For any r for which the sum over n has converged the oscillating Q_c^a clearly dominates over Q_c^b . As a result, there appears to be no chance for a cancellation between Q_c^a and Q_c^b by resummation of all Rydberg states.

The relations (59), (61), and (62) rely on the representation (50) for G_{nl} and thus on the completeness relation (15). One might ask how they have to be modified if one uses the same finite number of Rydberg states for the representation of G_{nl} as in E_c^{DD} . A direct analysis yields the asymptotic relations

$$\int_0^\infty dr' K(r,r') v_c(r') \sim 4(2I_F + 1) \frac{P_F(r) P_M(r)}{\epsilon_F - \epsilon_M} \times \int_0^\infty dr' P_F(r') P_M(r') v_c(r'), \quad (63)$$

$$Q_c^a(r) \sim \frac{P_{M-1}(r) P_M(r)}{\epsilon_{M-1} - \epsilon_M} \int_0^\infty dr' \left[P_M(r') \frac{\delta E_c}{\delta P_{M-1}(r')} - P_{M-1}(r') \frac{\delta E_c}{\delta P_M(r')} \right], \quad (64)$$

$$Q_c^b(r) \sim P_M(r)^2 \frac{\partial E_c}{\partial \epsilon_M}, \quad (65)$$

which do not depend on the specific form of the functional E_c . Again the left-hand and right-hand sides of the OPM equation decay differently, so that no solution is found, contradicting the basic assumption that v_c vanishes for $r \rightarrow \infty$. As before, resummation of all Rydberg states cannot cure this deficiency as indicated in Figs. 4 and 5 all quantities in Figs.

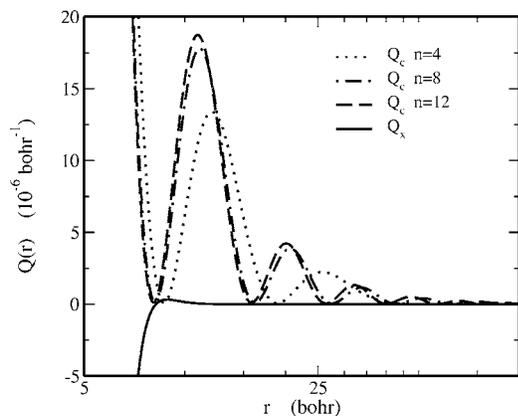


FIG. 4. As in Fig. 2, but G_{nl} constructed from a finite number of Rydberg states only.

4 and 5 have been evaluated from the exact KS states, obtained by finite-difference methods from the exact KS potential [39]—the differences resulting from use of self-consistent x-only states instead of the exact states are not visible in the plots).

One thus concludes that the potential obtained from large classes of orbital- and eigenvalue-dependent functionals—and in particular the potential resulting from E_c^{MP2} , diverges for large r —if only Rydberg states are included in the functional.

Given the fact that a first self-consistent application of E_c^{MP2} to atoms and small molecules within the framework of Gaussian basis sets can be found in the literature [40], one might ask about the implications of Eqs. (63)–(65) for basis set calculations. Clearly, a contradiction in a mathematical sense can only be established via Eqs. (63)–(65) if P_F and P_M are exact KS states. If one utilizes a basis set representation

$$P_{nl}(r) = \sum_{k=1}^M c_{nl}^k \eta_k(r), \quad (66)$$

in general all P_{nl} have some nonvanishing overlap with the most weakly decaying basis function η_M . Consequently, the

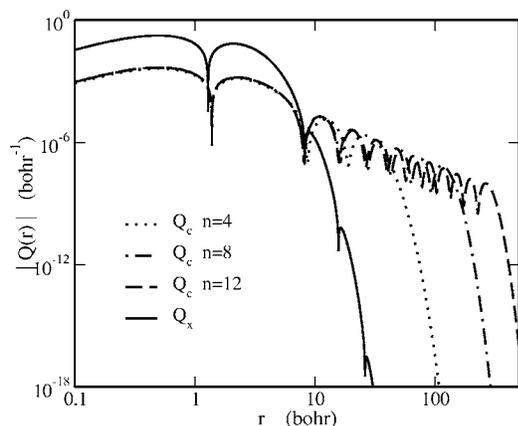


FIG. 5. As in Fig. 3, but G_{nl} constructed from a finite number of Rydberg states only.

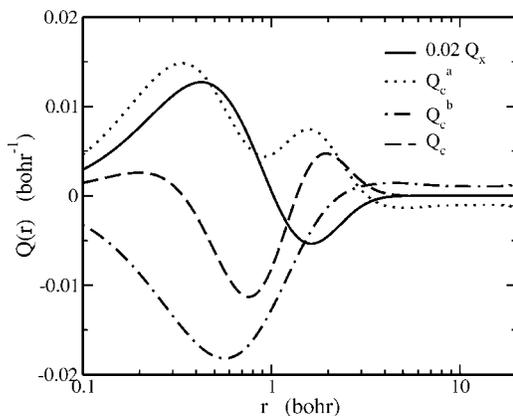


FIG. 6. Q_c for the He atom in a box: dependence of Q_c on the number of unoccupied Rydberg states included in E_c^{MP2} . For comparison also Q_x is plotted. The highest shell included is $n_{\text{max}}=300$ ($l_{\text{max}}=6$, $i_{\text{max}}=6400$). The box radius is chosen to be $R_0=20$ bohrs.

large- r behavior of all contributions to Eqs. (63)–(65) is identical and no contradiction can be deduced. However, the overlap of P_F with η_M will be much smaller than that of the highest unoccupied KS states. One could thus expect from Eqs. (63)–(65) that this imbalance between the amplitudes c_F^M and c_M^M has to be compensated for by a large expectation value $\int_0^\infty dr P_F(r) P_M(r) v_c(r)$. It remains to be investigated as to how far a (partial) cancellation between Q_c^a and Q_c^b for large r stabilizes the solution of the OPM equation in a basis set representation.

VI. ATOM IN BOX

In view of the results of Secs. IV and V the question about their compatibility with the findings of NFG arises. In order to answer this question one first of all has to notice that the argument of NFG relies on a Hilbert space with a completely discrete spectrum [32]. The most simple finite system which simulates this situation is an atom (characterized by the Coulomb potential of the nucleus) in a spherical cavity of radius R_0 (box), for which hard-wall boundary conditions are required at the box radius, $P_{nl}(R_0)=0$. In this case neither the conclusion of Sec. IV applies, as there are no continuum states in the spectrum, nor that of Sec. V, as now the sum over the discrete states is complete in the Hilbert space defined by the Hamiltonian plus boundary conditions; i.e., the completeness relation now reads

$$\sum_n P_{nl}(r) P_{nl}(r') = \delta(r - r'). \quad (67)$$

The results of a numerical study of the helium atom are given in Figs. 6–8. Figure 6 shows Q_c and its components as well as Q_x for a box radius of $R_0=20$ bohrs. All shells up to $n_{\text{max}}=300$ have been included in E_c^{MP2} (corresponding to $\epsilon_{n_{\text{max}}} \approx 1110$ hartrees), with the maximum angular momentum l_{max} of the unoccupied KS states restricted to 6 (higher momenta do not affect the results visibly). For G_{nl} the representation (50) has been utilized. The radial mesh, on which Eqs. (5) and (48) are solved by standard finite-difference

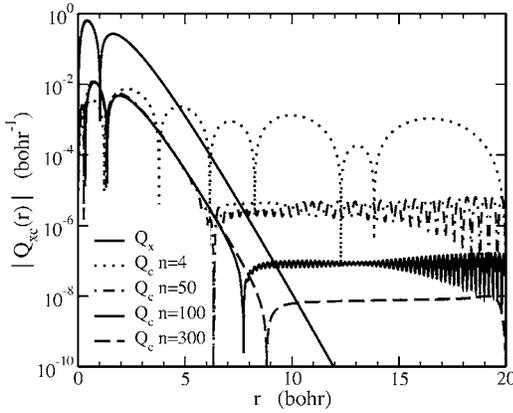


FIG. 7. Q_c for the He atom in a box: range of cancellation between Q_c^a and Q_c^b as a function of the number of unoccupied shells n included in E_c^{MP2} ($l_{\text{max}}=6$, $i_{\text{max}}=6400$).

methods, consists of $i_{\text{max}}=6400$ points, distributed logarithmically close to the nucleus and linearly in the asymptotic regime. All KS orbitals and eigenvalues have been generated by solution of Eq. (5) for the exact v_s obtained for a free helium atom [39] with the boundary condition $P_{nl}(r \geq R_0) = 0$.

Figure 6 is in marked contrast to the corresponding figure 2 for the free atom. On the scale used for Fig. 6, Q_c and Q_x decay similarly rapidly for large r . This result is intrinsically related to the cancellation between Q_c^a and Q_c^b , which individually approach a constant for large r . The range of r values for which Q_c^a and Q_c^b cancel systematically increases with the number of shells included in E_c^{MP2} , as demonstrated in Fig. 7. If only a few Rydberg-like shells are taken into account, the picture very much looks like that obtained for the free atom (Fig. 3). The more states are included the larger the range of r values becomes in which the decay of the total Q_c follows that of Q_x . For instance, for $n_{\text{max}}=50$ the synchronous decay is kept up to a critical radius r_{crit} of about 5 bohrs, while for $n_{\text{max}}=300$ the critical radius is shifted to almost 8 bohrs. At the same time, the amplitude and the period of the oscillations of Q_c observed for $r > r_{\text{crit}}$ reduce. In the case of the most refined numerical treatment the absolute values of the individual components Q_c^a and Q_c^b at r_{crit} are five orders of magnitude larger than their sum. One can thus consider Figs. 6 and 7 as a numerical proof for the cancellation between these two quantities. The high sensitivity of the cancellation between Q_c^a and Q_c^b to the degree of completeness achieved is nevertheless evident.

It seems worthwhile to point out that this sensitivity is much higher than that of E_c^{MP2} itself, as demonstrated in Table I. The MP2 energy is quite close to convergence already for $n_{\text{max}}=100$.

It remains to verify that the ratio between the total Q_c and Q_x actually approaches a constant for sufficiently large r : For the atom in the box to be a realistic simulation of the free atom one should be able to find a range of semiasymptotic r values for which Eq. (60) is satisfied. Figure 8 shows that in the range $r < r_{\text{crit}}$ this is in fact the case, as already suggested by Fig. 7 (which does not allow one to resolve powers of r due to its logarithmic scale). One thus concludes that the

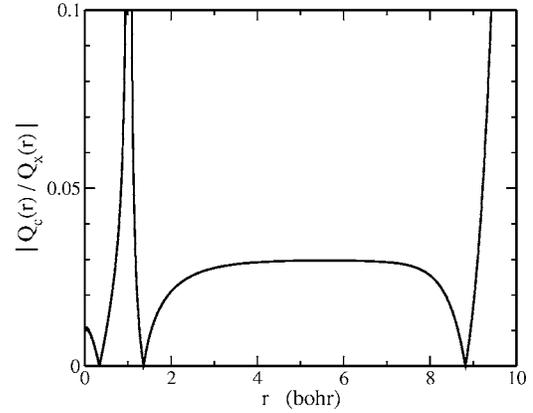


FIG. 8. Ratio (60) for the He atom in a box: results for the MP2 functional ($n_{\text{max}}=300$, $l_{\text{max}}=6$, $R_0=20$ bohrs).

solubility of the OPM equation for E_c^{MP2} relies on a discrete spectrum and on completeness in this countable Hilbert space. Any numerical solution of the OPM equation, which is necessarily based on a finite number of KS states, must be restricted to that region in space for which these states ensure a constant asymptotic ratio Q_c/Q_x . In fact, choosing both R_0 and n_{max} sufficiently large, one can devise a continuation scheme, which essentially allows the evaluation of v_c^{MP2} for free atoms from the results obtained for the atom in the box [36].

VII. TRANSITION FROM AN ATOM IN A BOX TO A FREE ATOM

Given the results of Secs. IV–VI one would like to understand the origin of the problem with the continuum states in more detail. Let us therefore finally analyze the transition from the atom in a box of radius R_0 to the free atom, corresponding to $R_0 \rightarrow \infty$. The first step of this analysis is a reformulation of the sum over positive-energy states as an integral over k , relying on the basic quantization condition and the large size of the box. Within this framework one can then express all relevant quantities as a function of R_0 , which finally allows one to take the limit $R_0 \rightarrow \infty$. This procedure is completely analogous to the transition from plane waves in a cubic box to free plane waves.

For the atom in the box one requires hard-wall boundary conditions

$$P_{nl}(R_0) = 0, \quad (68)$$

with R_0 understood to be much larger than the typical atomic size of 10 bohrs. For such R_0 the discrete positive-energy

TABLE I. Dependence of E_c^{MP2} on the number n_{max} of shells included for an atom in a box ($l_{\text{max}}=6$).

n_{max}	$\epsilon_{n_{\text{max}}}^{\text{MP2}}$ [hartree]	$-E_c^{\text{MP2}}$ [mhartree]
50	30.4	47.06
100	122.9	48.14
200	492.9	48.23
300	1109.7	48.24

solutions of Eq. (5) have the form (10) for all $r \gg 1$ bohr. For the positive-energy states the boundary condition (68) can thus be implemented on the basis of the asymptotic form (10),

$$k_{nl}R_0 + \frac{Zm}{k_{nl}} \ln(2k_{nl}R_0) - \frac{\pi}{2}l - \eta_{nl} = n\pi. \quad (69)$$

Equation (69) yields a discrete, countable positive-energy spectrum whose eigenenergies depend on the potential $v_s(r)$ via the phase shift. With increasing R_0 the spectrum becomes more and more dense, so that all sums over n can eventually be replaced by integrations over k_{nl} . The required density of states is obtained by differentiation of Eq. (69),

$$\frac{dk_{nl}}{dn} = \frac{\pi}{R_0} \left[1 - \frac{1}{R_0} \left(\frac{Zm}{k_{nl}^2} [1 - \ln(2k_{nl}R_0)] + \frac{d\eta_{nl}}{dk_{nl}} \right) \right]^{-1}. \quad (70)$$

As the accumulated phase shift η_{nl} does not increase linearly with R_0 (otherwise the orbitals would not approach their asymptotic form), one finds, in the limit of very large R_0 ,

$$\frac{dk}{dn} = \frac{\pi}{R_0}. \quad (71)$$

It is most convenient to renormalize the associated discrete positive-energy states in the box as

$$\int_0^{R_0} dr \bar{P}_{kl}(r)^2 = \frac{R_0}{\pi} \quad (72)$$

$$\Leftrightarrow \bar{P}_{kl}(r) = \left(\frac{R_0}{\pi} \right)^{1/2} P_{nl}(r). \quad (73)$$

In the limit $R_0 \rightarrow \infty$ these states approach exactly the corresponding continuum states (10) with their normalization (11). The normalization (73) has the advantage that in this limit the overlap between the \bar{P}_{kl} and the localized negative-energy orbitals (normalized to 1) remains constant. It thus allows the extraction of the R_0 dependence of all kinds of matrix elements, such as, for instance, the Slater integrals required for E_c^{MP2} . Combining the normalization (73) with the density of states (71) one can express sums over positive-energy states as

$$\sum_n \Theta(\epsilon_{nl}) P_{nl}(r) P_{n'l'}(r') \rightarrow \int_0^\infty dk \bar{P}_{kl}(r) \bar{P}_{k'l'}(r'). \quad (74)$$

On this basis one can now study the various quantities relevant for the OPM procedure. We start with decomposing the MP2 correlation energy of the discrete system in the spirit of Eqs. (32)–(35),

$$E_c^- = \sum_{\substack{n_1 n_2 n_3 n_4 \\ l_1 l_2 l_3 l_4}} \Theta(-\epsilon_{n_3 l_3}) \Theta(-\epsilon_{n_4 l_4}) \times \frac{N(n_1 l_1, n_2 l_2 | n_3 l_3, n_4 l_4)}{\epsilon_{n_1 l_1} + \epsilon_{n_2 l_2} - \epsilon_{n_3 l_3} - \epsilon_{n_4 l_4}}, \quad (75)$$

$$E_c^{++} = \sum_{\substack{n_1 n_2 n_3 n_4 \\ l_1 l_2 l_3 l_4}} \Theta(-\epsilon_{n_3 l_3}) \Theta(\epsilon_{n_4 l_4}) \frac{N(n_1 l_1, n_2 l_2 | n_3 l_3, n_4 l_4)}{\epsilon_{n_1 l_1} + \epsilon_{n_2 l_2} - \epsilon_{n_3 l_3} - \epsilon_{n_4 l_4}} \quad (76)$$

$$= \sum_{\substack{n_1 n_2 n_3 \\ l_1 l_2 l_3}} \int_0^\infty dk \frac{N(n_1 l_1, n_2 l_2 | n_3 l_3, \bar{k}l)}{\epsilon_{n_1 l_1} + \epsilon_{n_2 l_2} - \epsilon_{n_3 l_3} - \epsilon}, \quad (77)$$

$$E_c^{++} = \sum_{\substack{n_1 n_2 n_3 n_4 \\ l_1 l_2 l_3 l_4}} \Theta(\epsilon_{n_3 l_3}) \Theta(\epsilon_{n_4 l_4}) \frac{N(n_1 l_1, n_2 l_2 | n_3 l_3, n_4 l_4)}{\epsilon_{n_1 l_1} + \epsilon_{n_2 l_2} - \epsilon_{n_3 l_3} - \epsilon_{n_4 l_4}} \quad (78)$$

$$= \sum_{n_1 n_2} \int_0^\infty dk \int_0^\infty dk' \frac{N(n_1 l_1, n_2 l_2 | \bar{k}l, \bar{k}'l')}{\epsilon_{n_1 l_1} + \epsilon_{n_2 l_2} - \epsilon - \epsilon'}, \quad (79)$$

where $\bar{k}l$ abbreviates the use of the rescaled states (73) inside the Slater integrals [$(N(n_1 l_1, n_2 l_2 | n_3 l_3, \bar{k}l))$ absorbs a factor of R_0/π as it contains the product of two positive-energy states]. In their rescaled form (77) and (79) the energies are free of any overall R_0 dependence, so that, for $R_0 \rightarrow \infty$, E_c^{++} and E_c^{--} directly approach their continuum limits (34) and (35). The normalization (73) ensures that the overlap between negative- and positive-energy states remains finite in the limit $R_0 \rightarrow \infty$.

Let us now consider the ingredients of the OPM equation (16). Its left-hand side can be easily expressed in an R_0 -independent way by use of the representation (50) inside the kernel (21). As is clear from Eq. (47), the crucial quantity to be studied is the inhomogeneity. Let us first discuss Q_c^a , with a decomposition into one part resulting from derivatives with respect to negative-energy states and the remainder,

$$Q_c^a(r) = Q_{c,-}^a(r) + Q_{c,+}^a(r), \quad (80)$$

$$Q_{c,\pm}^a(r) = - \sum_{nl} \Theta(\pm \epsilon_{nl}) P_{nl}(r) \int_0^{R_0} dr' G_{nl}(r, r') \frac{\delta E_c^{\text{MP2}}}{\delta P_{nl}(r')}, \quad (81)$$

with the Green's function for a purely discrete spectrum,

$$G_{nl}(r, r') = \sum_{n' \neq n} \frac{P_{n'l}(r) P_{n'l}(r')}{\epsilon_{n'l} - \epsilon_{nl}}. \quad (82)$$

In the limit $R_0 \rightarrow \infty$ $Q_{c,-}^a$ approaches Eq. (26) [with G_{nl} most easily represented via Eq. (50)], so that further discussion is not necessary. $Q_{c,+}^a$ can be evaluated by use of the relations collected in Appendix C. Insertion of Eqs. (77), (82), and (C2) into Eq. (81) yields

$$Q_{c,+}^{a,-+}(r) = - \sum_{nl} \Theta(\epsilon_{nl}) \sum_{n' \neq n} \frac{P_{nl}(r)P_{n'l}(r)}{\epsilon_{n'l} - \epsilon_{nl}} \times \sum_{\substack{n_1 n_2 n_3 \\ l_1 l_2 l_3}} \frac{N(n_1 l_1, n_2 l_2 | n_3 l_3, nl/n'l)}{\epsilon_{n_1 l_1} + \epsilon_{n_2 l_2} - \epsilon_{n_3 l_3} - \epsilon_{nl}}, \quad (83)$$

with $N(n_1 l_1, n_2 l_2 | n_3 l_3, nl/n'l)$ defined by Eq. (C3). An analogous expression is obtained for $Q_{c,+}^{a,++}$ resulting from E_c^{++} , which is suppressed for brevity. At this point it is straightforward to introduce the rescaling (73) and the accompanying k integration (74), valid for large R_0 ,

$$Q_{c,+}^{a,-+}(r) = - \int_0^\infty dk \sum_l \sum_{n'} \Theta(-\epsilon_{n'l}) \frac{\bar{P}_{kl}(r)P_{n'l}(r)}{\epsilon_{n'l} - \epsilon} \times \sum_{\substack{n_1 n_2 n_3 \\ l_1 l_2 l_3}} \frac{N(n_1 l_1, n_2 l_2 | n_3 l_3, \bar{k}l/n'l)}{\epsilon_{n_1 l_1} + \epsilon_{n_2 l_2} - \epsilon_{n_3 l_3} - \epsilon} - \int_0^\infty dk \sum_l \mathcal{P} \int_0^\infty dk' \frac{\bar{P}_{kl}(r)\bar{P}_{k'l}(r)}{\epsilon' - \epsilon} \times \sum_{\substack{n_1 n_2 n_3 \\ l_1 l_2 l_3}} \frac{N(n_1 l_1, n_2 l_2 | n_3 l_3, \bar{k}l/k'l)}{\epsilon_{n_1 l_1} + \epsilon_{n_2 l_2} - \epsilon_{n_3 l_3} - \epsilon}. \quad (84)$$

In the limit $R_0 \rightarrow \infty$, $Q_{c,+}^{a,-+}$ (together with $Q_{c,+}^{a,++}$) approaches the continuum limit (27). In this limit the two contributions on the right-hand side of Eq. (84) can be combined by use of the Green's function (22). From its discrete origin, but also from the expression (84) it is immediately clear that $Q_{c,+}^{a,-+}$ satisfies the sum rule (42).

It remains to examine the critical eigenvalue-derivative term Q_c^b . Decomposing Q_c^b into derivatives with respect to negative and positive energies,

$$Q_{c,\pm}^b(r) = \sum_{nl} \Theta(\pm \epsilon_{nl}) P_{nl}(r)^2 \frac{\partial E_c^{\text{MP2}}}{\partial \epsilon_{nl}}, \quad (85)$$

and introducing the rescaling (73) of the positive-energy states, one obtains

$$Q_{c,-}^{b,-+}(r) = -2 \sum_{\substack{n_1 n_2 n_3 n_4 \\ l_1 l_2 l_3 l_4}} \Theta(-\epsilon_{n_3 l_3}) \Theta(-\epsilon_{n_4 l_4}) \times [P_{n_1 l_1}(r)^2 - P_{n_3 l_3}(r)^2] \times \frac{N(n_1 l_1, n_2 l_2 | n_3 l_3, n_4 l_4)}{(\epsilon_{n_1 l_1} + \epsilon_{n_2 l_2} - \epsilon_{n_3 l_3} - \epsilon_{n_4 l_4})^2}, \quad (86)$$

$$Q_{c,-}^{b,+}(r) = - \sum_{\substack{n_1 n_2 n_3 \\ l_1 l_2 l_3 l}} [P_{n_1 l_1}(r)^2 + P_{n_2 l_2}(r)^2 - P_{n_3 l_3}(r)^2] \times \int_0^\infty dk \frac{N(n_1 l_1, n_2 l_2 | n_3 l_3, \bar{k}l)}{(\epsilon_{n_1 l_1} + \epsilon_{n_2 l_2} - \epsilon_{n_3 l_3} - \epsilon)^2}, \quad (87)$$

$$Q_{c,-}^{b,++}(r) = -2 \sum_{\substack{n_1 n_2 \\ l_1 l_2}} P_{n_1 l_1}(r)^2 \sum_{l'l''} \int_0^\infty dk \int_0^\infty dk' \times \frac{N(n_1 l_1, n_2 l_2 | \bar{k}l, \bar{k}'l')}{(\epsilon_{n_1 l_1} + \epsilon_{n_2 l_2} - \epsilon - \epsilon')^2}, \quad (88)$$

$$Q_{c,+}^{b,-+}(r) = 0, \quad (89)$$

$$Q_{c,+}^{b,+}(r) = \frac{\pi}{R_0} \sum_l \int_0^\infty dk \bar{P}_{kl}(r)^2 \times \sum_{\substack{n_1 n_2 n_3 \\ l_1 l_2 l_3}} \frac{N(n_1 l_1, n_2 l_2 | n_3 l_3, \bar{k}l)}{(\epsilon_{n_1 l_1} + \epsilon_{n_2 l_2} - \epsilon_{n_3 l_3} - \epsilon)^2}, \quad (90)$$

$$Q_{c,+}^{b,++}(r) = \frac{2\pi}{R_0} \sum_{l'l''} \int_0^\infty dk \bar{P}_{kl}(r)^2 \int_0^\infty dk' \times \sum_{\substack{n_1 n_2 \\ l_1 l_2}} \frac{N(n_1 l_1, n_2 l_2 | \bar{k}l, \bar{k}'l')}{(\epsilon_{n_1 l_1} + \epsilon_{n_2 l_2} - \epsilon - \epsilon')^2}. \quad (91)$$

Consequently, for $R_0 \rightarrow \infty$ $Q_{c,-}^b$ approaches the Rydberg term (28), while $Q_{c,+}^{b,-+}$ and $Q_{c,+}^{b,++}$ vanish. In the limit $R_0 \rightarrow \infty$ the norm of the unscaled positive-energy states P_{nl} and thus $Q_{c,+}^b$ vanishes in any finite region of space.

On the other hand, upon integration over the complete box one finds, from Eq. (90),

$$\int_0^{R_0} dr Q_{c,+}^{b,-+}(r) = \int_0^\infty dk \sum_{\substack{n_1 n_2 n_3 \\ l_1 l_2 l_3 l}} \frac{N(n_1 l_1, n_2 l_2 | n_3 l_3, \bar{k}l)}{(\epsilon_{n_1 l_1} + \epsilon_{n_2 l_2} - \epsilon_{n_3 l_3} - \epsilon)^2}, \quad (92)$$

so that the integral over $Q_{c,+}^{b,-+}$ is nonzero also in the limit $R_0 \rightarrow \infty$: The linearly increasing regime of integration compensates for the local decay of $Q_{c,+}^{b,-+}$. The same is true for $Q_{c,+}^{b,++}$. One thus ends up with the statement

$$\lim_{R_0 \rightarrow \infty} \int_0^{R_0} dr Q_{c,+}^b(r) \neq \int_0^\infty dr \lim_{R_0 \rightarrow \infty} Q_{c,+}^b(r) = 0. \quad (93)$$

By comparison with Eqs. (45) and (46) one verifies that Eq. (92) together with its $Q_{c,+}^{b,++}$ counterpart provides exactly the contributions required to satisfy the sum rule

$$\int_0^\infty dr Q_{c,+}^b(r) = 0. \quad (94)$$

In view of Eq. (93) one concludes that the OPM equation cannot be solved after the continuum limit has been taken for its ingredients. Any practical realization has to ensure a countable spectrum by suitable boundary conditions, even if eventually the limit of a free system is of interest.

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APPENDIX A: NORMALIZATION OF POSITIVE ENERGY STATES

In this appendix the norm of the continuum states (10) inside a sphere of radius R is explicitly evaluated. Provided that R is sufficiently large, the deviations of the true \bar{P}_{kl} from its asymptotic form (10), which one finds for small r , are irrelevant for the normalization integral, so that one obtains

$$\int_0^R dr \bar{P}_{kl}(r)^2 = \frac{2}{\pi} \int_0^R dr \sin[f(r)]^2 + \dots, \quad (\text{A1})$$

with the abbreviation

$$f(r) = kr + \frac{Zm}{k} \ln(2kr) - \frac{\pi}{2}l - \eta_{kl}. \quad (\text{A2})$$

This integral is easily evaluated for $Z=0$,

$$\begin{aligned} \int_0^R dr \sin \left[kr - \frac{\pi}{2}l - \eta_{kl} \right]^2 \\ = \frac{R}{2} + \frac{1}{2k} \cos[kR - \pi l - 2\eta_{kl}] \sin[kR], \end{aligned} \quad (\text{A3})$$

but requires more care for $Z \neq 0$. With

$$f'(r) = k + \frac{Zm}{kr}, \quad (\text{A4})$$

$$f''(r) = -\frac{Zm}{kr^2}, \quad (\text{A5})$$

one can apply partial integration in the form

$$\begin{aligned} \int_0^R dr \sin[f(r)]^2 &= - \int_0^R dr \frac{\sin[f(r)]}{f'(r)} \frac{d}{dr} \cos[f(r)] \\ &= - \frac{\sin[f(r)] \cos[f(r)]}{f'(r)} \Big|_0^R \\ &\quad + \int_0^R dr \cos[f(r)] \left[\cos[f(r)] \right. \\ &\quad \left. - \frac{f''(r)}{f'(r)^2} \sin[f(r)] \right]. \end{aligned}$$

Insertion of Eqs. (A2), (A4), and (A5) then leads to

$$\begin{aligned} 2 \int_0^R dr \sin[f(r)]^2 &= R - \frac{\sin[f(R)] \cos[f(R)]}{k + Zm/(kR)} \\ &\quad + \int_0^R dr \frac{kZm}{[k^2r + Zm]^2} \sin[f(r)] \cos[f(r)]. \end{aligned} \quad (\text{A6})$$

For large R the second and third terms on the right-hand side of Eq. (A6) remain finite, so that they are negligibly small compared to the first term. The same is true for the corresponding term in Eq. (A3), so that, including the prefactor of $2/\pi$ in Eq. (A1), one ends up with Eq. (11).

APPENDIX B: BASIC FUNCTIONAL DERIVATIVES OF KS ORBITALS

In this appendix the functional derivatives of the KS states and eigenvalues which enter the OPM equation are explicitly evaluated for a system with a partially continuous spectrum. As in the case of a purely discrete spectrum [5], the functional derivative of the discrete KS states, $\delta P_{nl}(r') / \delta v_s(r)$, is most conveniently evaluated by analyzing the response δP_{nl} of P_{nl} to a small variation δv_s of the KS potential in the radial equation (4). To first order one obtains

$$[\hat{T}_l + v_s(r) - \epsilon_{nl}] \delta P_{nl}(r) = [\delta \epsilon_{nl} - \delta v_s(r)] P_{nl}(r). \quad (\text{B1})$$

Multiplication by P_{nl} , use of Eq. (4), and subsequent integration then yield the familiar result [5]

$$\delta \epsilon_{nl} = \int_0^\infty dr P_{nl}(r)^2 \delta v_s(r), \quad (\text{B2})$$

which provides the basis for Eq. (28). The relation between δP_{nl} and δv_s can be established by use of the Green's function G_{nl} which satisfies the differential equation (23). In fact, it is straightforward to demonstrate that

$$\delta P_{nl}(r) = - \int_0^\infty dr' G_{nl}(r, r') P_{nl}(r') \delta v_s(r') \quad (\text{B3})$$

satisfies Eq. (B1) together with the constraint of norm conservation,

$$\int_0^\infty dr P_{nl}(r) \delta P_{nl}(r) = 0. \quad (\text{B4})$$

Equation (B3) directly leads to Eqs. (21) and (26).

This procedure has to be modified slightly in the case of continuum states. For any energy ϵ from the continuous part of the spectrum one finds a solution of Eq. (9) also after switching on the perturbation δv_s . The radial equation for given ϵ thus reads, to first order,

$$\left\{ \hat{T}_l + v_s(r) - \frac{k^2}{2m} \right\} \delta \bar{P}_{kl}(r) = - \delta v_s(r) \bar{P}_{kl}(r). \quad (\text{B5})$$

Relying on the differential equation (30) one thus finds

$$\delta\bar{P}_{kl}(r) = - \int_0^\infty dr' G_{kl}(r, r') \bar{P}_{kl}(r') \delta v_s(r'). \quad (\text{B6})$$

Equation (B6) provides the background for Eq. (27).

APPENDIX C: BASIC FUNCTIONAL DERIVATIVES OF SLATER INTEGRALS

In this Appendix we collect a number of relations required for the evaluation of Q_c^a for the case of E_c^{MP2} . First consider the functional derivative of the basic Slater integral (39) with respect to some orbital,

$$\begin{aligned} & \int_0^{R_0} dr P_{n'l'}(r) \frac{\delta}{\delta P_{nl}(r)} (n_1 l_1, n_2 l_2 | n_3 l_3, n_4 l_4)_L \\ &= \delta_{n_1 n} \delta_{l_1 l} (n' l', n_2 l_2 | n_3 l_3, n_4 l_4)_L \\ &+ \delta_{n_2 n} \delta_{l_2 l} (n_1 l_1, n' l' | n_3 l_3, n_4 l_4)_L \\ &+ \delta_{n_3 n} \delta_{l_3 l} (n_1 l_1, n_2 l_2 | n' l', n_4 l_4)_L \\ &+ \delta_{n_4 n} \delta_{l_4 l} (n_1 l_1, n_2 l_2 | n_3 l_3, n' l')_L, \end{aligned} \quad (\text{C1})$$

where we have used the box radius R_0 as upper limit for the r integration. For all relations of this appendix, however, R_0 could be equal to infinity. From (C1) one obtains, for the complete numerator of the MP2 functional,

$$\begin{aligned} & \int_0^{R_0} dr P_{n'l'}(r) \frac{\delta}{\delta P_{nl}(r)} N(n_1 l_1, n_2 l_2 | n_3 l_3, n_4 l_4) \\ &= \delta_{n_1 n} \delta_{l_1 l} N(n l / n' l', n_2 l_2 | n_3 l_3, n_4 l_4) \\ &+ \delta_{n_2 n} \delta_{l_2 l} N(n_1 l_1, n l / n' l' | n_3 l_3, n_4 l_4) \\ &+ \delta_{n_3 n} \delta_{l_3 l} N(n_1 l_1, n_2 l_2 | n l / n' l', n_4 l_4) \end{aligned}$$

$$+ \delta_{n_4 n} \delta_{l_4 l} N(n_1 l_1, n_2 l_2 | n_3 l_3, n l / n' l'), \quad (\text{C2})$$

with the abbreviation

$$\begin{aligned} N(1/1', 2|3, 4) &= \Theta_1 \Theta_2 (1 - \Theta_3) (1 - \Theta_4) \\ &\times [D(1/1', 2|3, 4) - X(1/1', 2|3, 4)] \end{aligned} \quad (\text{C3})$$

$$\begin{aligned} D(1/1', 2|3, 4) &= 4 \sum_{L=0}^{\infty} (l_1 0 l_3 0 | L 0)^2 (l_2 0 l_4 0 | L 0)^2 \\ &\times (1' 2 | 3 4)_L (1 2 | 3 4)_L \\ &\times \frac{(2l_1 + 1)(2l_2 + 1)(2l_3 + 1)(2l_4 + 1)}{(2L + 1)^3} \end{aligned} \quad (\text{C4})$$

$$\begin{aligned} X(1/1', 2|3, 4) &= \sum_{L, L'=0}^{\infty} (-1)^{l_1 + l_2 + l_3 + l_4 + L + L'} W(l_1 l_3 l_4 l_2; L L') \\ &\times [(1' 2 | 3 4)_L (1 2 | 4 3)_{L'} + (1 2 | 3 4)_L (1' 2 | 4 3)_{L'}] \\ &\times (l_1 0 l_3 0 | L 0) (l_2 0 l_4 0 | L 0) (l_1 0 l_4 0 | L' 0) \\ &\times (l_2 0 l_3 0 | L' 0) \\ &\times \frac{(2l_1 + 1)(2l_2 + 1)(2l_3 + 1)(2l_4 + 1)}{(2L + 1)(2L' + 1)}. \end{aligned} \quad (\text{C5})$$

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