

Multicenter-type corrections to standard DFT exchange and correlation functionals

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We propose to express corrections to the standard approximations of the exchange-correlation functionals in the form of multiatom-centered functionals that can be related to the atoms-in-molecules theory of Bader and a multicenter density expansion. Unlike conventional functionals, the variables of these multicenter functionals are the positions and identities of the nuclei, which can unambiguously be determined from the topology of the electronic density. The proposed multicenter correction is used to provide a theoretical basis for the dispersion-corrected atom-centered potential (DCACP) approach used to improve van der Waals interactions in conventional density functional theory. Convergence to the correct long-range asymptotic behavior of the multicenter expansion for DCACPs is demonstrated in the test case of the H₂ van der Waals dimer.

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Multicenter expansions of classical and quantum fields, such as densities and wave functions, have been exploited in many electronic structure theories.^{1–4} The centers of the expansion are most commonly chosen to coincide with the positions of the atoms in the system. A similar approach was followed by Nagy *et al.*⁵ for the derivation of density functional formulas in terms of moments of the electron density.

In this paper, we apply similar techniques to propose a multiatom-centered expansion for corrections to the approximate exchange-correlation functionals in density functional theory (DFT). In this case, the particular choice for such an expansion is physically intuitive since deviations from the homogeneous electron-gas reference are largest at the atoms. Specifically, the total electronic density of a system can be regarded as a sum of the atomic densities corrected for the interatomic interactions.¹ Some of the topological properties of the atomic densities are preserved even upon formation of molecules and solids: for example, the locations of the density maxima and the cusps that are uniquely associated with the positions of the atoms.^{6–9} In view of this, it is natural to derive a multicenter-expansion-based scheme for the optimization of density functionals that are based on the topology of the total electronic density.

We first introduce the concept of reformulating corrections to the approximate universal density functionals [Eq. (2)] as a multicenter functional, drawing largely from the idea of multicenter density expansions.⁴ Using the atoms-in-molecules theory of Bader,¹⁰ we argue that all quantities required for the functional, i.e., the positions and the charges of the nuclei in a system, can be uniquely derived from the electronic charge density. The approach of atom-centered potentials (ACPs) is briefly recapped before we switch our focus to one particular category of ACPs, dispersion-corrected atom-centered potentials (DCACPs). The convergence of the multicenter expansion for DCACPs is demonstrated by an essentially exact reproduction of the asymptotic r^{-6} behavior when a sufficiently complete (spherical harmonics and/or Gaussian functions) basis is employed.

Here, we present the concept of multicenter density functionals. In DFT, the basic variable is the electron density $\rho(\mathbf{r})$, a function of three spatial coordinates (and, for spin polarized systems, the spin). Given a density, the following relation,

$$E[\rho] = F[\rho] + \int d\mathbf{r} v_{\text{ext}}(\mathbf{r})\rho(\mathbf{r}), \quad (1)$$

delivers the corresponding energy and, upon minimization, the ground-state density and energy. $F[\rho]$ is a universal functional which does not depend explicitly on the external potential $v_{\text{ext}}(\mathbf{r})$. Even though such a functional exists, its exact form is still elusive, and many studies have been devoted to the search for better approximations. One can rewrite the exact universal functional $F[\rho]$ as the sum of an approximate form commonly adopted by the DFT community ($F^{\text{approx}}[\rho]$) and a correction term ($\Delta F[\rho]$) with respect to $F[\rho]$,

$$F[\rho] = F^{\text{approx}}[\rho] + \Delta F[\rho]. \quad (2)$$

Instead of a conventional functional form for $\Delta F[\rho]$, we propose to utilize a multicenter expansion of the form $\Delta F^{\text{MC}}[\rho](\{\mathbf{R}_j\}_{j=1}^M)$, in which \mathbf{R}_j is defined with respect to site j with position vector \mathbf{R}_j . We shall closely follow the argument presented by Averill and Painter⁴ who considered the decomposition of the charge density into a sum of atom-centered functions. Here, we only consider functionals of the form $\Delta F[\rho] = \int d\mathbf{r} \rho(\mathbf{r}) \Delta \tilde{F}(\mathbf{r})$ and their nonlocal equivalent $\Delta F[\rho] = \int d\mathbf{r} \int d\mathbf{r}' \rho(\mathbf{r}) \Delta \tilde{F}(\mathbf{r}, \mathbf{r}') \rho(\mathbf{r}')$, where the functions $\Delta \tilde{F}(\mathbf{r})$ and $\Delta \tilde{F}(\mathbf{r}, \mathbf{r}')$ are expanded in a multicenter fashion and can also depend (in the most general case) on the electronic density ρ .

Using the projection technique pioneered by Boys and Rajagopal,¹ and further refined by Becke² and Delley,³ $\Delta \tilde{F}(\mathbf{r})$ can be written as a sum of site- j -centered functions P_j ,

$$\Delta \tilde{F}(\mathbf{r}) \approx \sum_{j=1}^M \Delta \tilde{f}_j(\mathbf{r}) = \sum_{j=1}^M P_j(\mathbf{r}_j), \quad (3)$$

where $\mathbf{r}_j = \mathbf{r} - \mathbf{R}_j$.

P_j was originally defined by a set of weight functions Γ_j also centered at site j ,

$$P_j(\mathbf{r}_j) = \Gamma_j(\mathbf{r}_j) \Delta \tilde{F}(\mathbf{r}), \quad (4)$$

where for any \mathbf{r} ,

$$\sum_j \Gamma_j(\mathbf{r}) = 1. \quad (5)$$

One possible choice for Γ_j can be the homonuclear fuzzy-cell function of Becke.² In this scheme, each Γ_j has a value of unity in the vicinity of its own nucleus but vanishes in a continuous and well-behaved manner near any other nucleus. The system is thus divided into fuzzy, overlapping analytically continuous cells. Applying Γ_j to $\Delta\tilde{F}(\mathbf{r})$ produces P_j that is large in magnitude near site j and approaches zero away from site j .

An alternative and probably more general way of obtaining multicentered functional corrections is achieved using the convolution of atom-centered volume functions Γ_j with a given functional correction $\Delta\tilde{F}'$,

$$\Delta\tilde{F}(\mathbf{r}) = \sum_{j=1}^M P_j(\mathbf{r}_j) = \sum_{j=1}^M \int d\mathbf{r} \Gamma_j(\mathbf{r}_j - \mathbf{r}) \Delta\tilde{F}'(\mathbf{r}). \quad (6)$$

This partitioning of the overall functional correction $\Delta\tilde{F}(\mathbf{r})$ into different atomic contributions is simpler to handle than the one suggested in Eq. (4) and does not require the additional constraint given in Eq. (5). Furthermore, this partitioning has a straightforward generalization to the nonlocal case,

$$\begin{aligned} \Delta\tilde{F}(\mathbf{r}, \mathbf{r}') &= \sum_{j=1}^M P_j(\mathbf{r}_j, \mathbf{r}'_j) \\ &= \sum_{j=1}^M \int d\mathbf{r} d\mathbf{r}' \Gamma_j(\mathbf{r}_j - \mathbf{r}) \Delta\tilde{F}'(\mathbf{r}, \mathbf{r}') \Gamma_j(\mathbf{r}'_j - \mathbf{r}'). \end{aligned} \quad (7)$$

At this point, it is convenient to carry out a spherical harmonics expansion about the sites j . The harmonics coefficients,

$$p_{\ell m}(r_j) = \int Y_{\ell m}(\hat{\mathbf{r}}_j) P_j(\mathbf{r}_j) d\Omega, \quad (8)$$

determine the approximate representation of P_j ,

$$P_j(\mathbf{r}_j) \approx \sum_{\ell=0}^{\ell_{\max}} \sum_{m=-\ell}^{+\ell} Y_{\ell m}(\hat{\mathbf{r}}_j) p_{\ell m}(r_j), \quad (9)$$

where $d\Omega$ is the angular volume element centered at j , and the accuracy of the expansion is controlled solely by the cutoff value ℓ_{\max} .

In the nonlocal case,

$$P_j(\mathbf{r}_j, \mathbf{r}'_j) \approx \sum_{\ell=0}^{\ell_{\max}} \sum_{m=-\ell}^{+\ell} \sum_{p=0}^{p_{\max}} \sum_{q=-p}^{+p} Y_{\ell m}(\hat{\mathbf{r}}_j) p_{\ell m, pq}(r_j, r'_j) Y_{pq}^*(\hat{\mathbf{r}}'_j), \quad (10)$$

where (see Appendix)

$$p_{\ell m, pq}(r_j, r'_j) = \frac{4\pi}{2\ell + 1} \gamma_{\ell 0}(r_j) \Delta\tilde{f}'_{\ell m, pq}(r_j, r'_j) \gamma_{\ell 0}(r'_j), \quad (11)$$

and $\gamma_{\ell 0}$ and $\Delta\tilde{f}'_{\ell m, pq}$ are the spherical harmonics coefficients of the weighting function Γ and of the functional correction $\Delta\tilde{F}'$, respectively.

In the following, we will consider the case of an orbital-dependent multicenter correction. Since the Kohn-Sham orbitals are functionals of the electron density, this can be seen as a natural and potentially advantageous formulation in the same spirit as optimized effective potentials.¹¹ In addition, it offers the possibility of linking this development with the recently introduced DCACP approach,¹² which has the following functional form:

$$\Delta F[\{\phi_i\}] = \sum_i \int \int d\mathbf{r} d\mathbf{r}' \phi_i(\mathbf{r}) \left\{ \sum_j P_j(\mathbf{r}_j, \mathbf{r}'_j) \right\} \phi_i^*(\mathbf{r}'), \quad (12)$$

where i runs through the occupied Kohn-Sham orbitals. This is the proposed orbital-dependent-functional form we will use to expand $\Delta F[\rho]$ in Eq. (2).

Multiatom-center functionals are uniquely defined by the density ρ only. The site j in the multicenter scheme is most commonly (and naturally) chosen to be the location of atom I in the system. One thus requires knowledge of the positions (and sometimes the charges) of the nuclei for evaluating multicenter functionals. To be uniquely defined by the electron density, these two pieces of information should be defined by ρ and ρ only; in other words, the following requirements need to be satisfied: (a) the topology of $\rho(\mathbf{r})$ (in particular the position of the cusps) uniquely determines the positions of the multicenter expansion $\{\mathbf{R}_j\}_{j=1}^M$ ^{8,10}; (b) for any given choice of I -centered weight function Γ_I , requirement (a) determines the projection $p_{\ell m}^I(r)$; and (c) a one-to-one mapping exists between Z_I and $\rho(\mathbf{R}_I)$, where Z_I is the nuclear charge at atom I .

Following the atoms-in-molecules theory of Bader,¹⁰ the atomic fragments in molecular systems are determined on the basis of the topology of the total electron density alone. The electronic charge density exhibits a cusp at the position of a nucleus in both the ground and excited states of many-electron systems.¹³ This condition can be used to describe the mapping required in condition (a).

Regarding requirement (c), the value of the charge density at nuclear position $\rho(\mathbf{R}_I)$ is much larger than its value at any other of its extrema except for protons. $\rho(\mathbf{R}_I)$ of a free atom in the Hartree-Fock approximation is roughly proportional to Z^3 for $Z < 55$ (Z is the atomic number) as depicted in Fig. 1.¹⁴ On the other hand, values of ρ at the saddle or bond critical points between given pairs of nuclei over the range of chemically significant internuclear separations range between $0 \leq \rho \leq 1.0$ a.u.,¹⁰ of considerably smaller magnitude than $\rho(\mathbf{R}_I)$. This universal mapping still holds in most chemical and physical electronic structure approaches, particularly in those in which the frozen-core approximation is invoked.

Furthermore, Kato's theorem⁶ states that

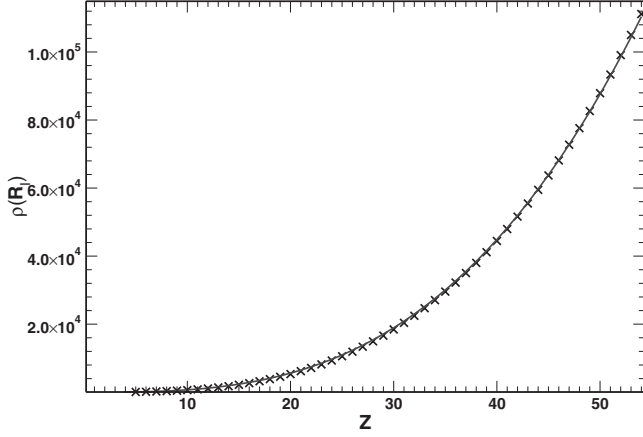


FIG. 1. Value of spherically averaged single-particle density at nucleus [symbol \times , $\rho(\mathbf{R}_I)$ in a.u.] as a function of the atomic number Z for all neutral atoms with $Z < 55$ in the Hartree-Fock approximation. Data are taken from Ref. 14. The line is a cubic fit through the data ($y = 0.7x^3$).

$$Z_I = - \left. \frac{1}{2\rho(\mathbf{r})} \frac{\partial \rho(\mathbf{r})}{\partial r} \right|_{\mathbf{r}=\mathbf{R}_I}, \quad (13)$$

where the partial derivatives are taken at the nuclei I . DFT shows that, in principle, knowledge of the ground-state electron density is sufficient to determine all molecular properties.⁷ The cusps of the density thus tell us where the nuclei are (\mathbf{R}_I) and what the atomic numbers Z_I are. We can therefore consider both the nuclear charge $Z_I[\rho]$ and the nuclear positions $\mathbf{R}_I[\rho]$ as functionals of the electronic density.

By replacing the positions of the multicenter expansion of $\Delta\tilde{F}(\mathbf{r}, \mathbf{r}')$ [Eq. (7)] with the nuclear positions \mathbf{R}_I , we introduce a density functional dependence through $Z_I[\rho]$ and $\mathbf{R}_I[\rho]$, leading to $\Delta\tilde{F}[\rho](\mathbf{r}, \mathbf{r}')$. However, in order to simplify the notation, in the following, we will drop the explicit density functional dependency from $\Delta\tilde{F}$ and all their spherical harmonics components. It is also worth mentioning that, since the functional derivative of $Z_I[\rho]$ and $\mathbf{R}_I[\rho]$ with respect to $\rho(\mathbf{r})$ is zero by definition (we do not consider here alchemical changes), the calculation of the correction potential, $v_{xc}^c(\mathbf{r}) = \Delta F[\rho] / \delta \rho(\mathbf{r})$, only involves the explicit functional derivative of $\Delta F[\rho] = \int d\mathbf{r}' \int d\mathbf{r}'' \rho(\mathbf{r}) \Delta\tilde{F}(\mathbf{r}, \mathbf{r}') \rho(\mathbf{r}'')$.

In conclusion, given any (even approximate) density of a many-electron system constructed from a sum of atomic densities (with a correct representation of the cusp. This is best achieved by either taking the atomic core density or through a reconstruction of the density at the cusp.¹⁵) and optimized according to any *ab initio* approach, it is possible to unambiguously locate all atomic positions (\mathbf{R}_I) in the system and to identify their corresponding physical nature (Z_I) on the basis of the electron-density distribution only. Therefore, any functional that depends explicitly on the atomic positions can, in principle, be recast into a density-only (i.e., “universal”) form.

We have demonstrated that the correction term $\Delta F[\rho(\mathbf{r})]$ can be projected into a multiatom-centered functional

$\Delta F^{\text{MC}}[\rho](\{\mathbf{R}_j\}_{j=1}^M)$ (herein referred to as ACF). This correction term can, in principle, be derived from theory but this is almost as difficult as searching for the true universal functional, $F[\rho]$. Alternatively, one can also empirically tune the ACF against some well-defined penalty functionals to improve the atomic or molecular properties of interest.¹⁶ To this end, we have used an analytic form similar to the one proposed by Goedecker *et al.*¹⁷ in the context of atomic pseudopotentials. These atom-centered analytic functions can be tuned to reach an accuracy that is on par with high-level *ab initio* calculations or simply functionals of higher rank for specific properties. Among others, this approach has been used, e.g., for generating link atoms to bridge the quantum and classical fragments in quantum mechanics/molecular mechanics simulations, designed in such a way that the link atoms minimally perturb the electronic structure in the quantum-mechanical region,¹⁶ for reproducing the electron density and derived molecular properties of hybrid functional quality within BLYP calculations,¹⁶ and for improving the description of dispersion forces in DFT (dispersion-corrected atom-centered potentials).¹²

ACFs employed in the above-mentioned studies are generally defined as

$$P_I(\mathbf{r}_I, \mathbf{r}'_I) = v_I^{\text{ACF}}(\mathbf{r}, \mathbf{r}') \\ = \sum_{\ell=0}^{\ell_{\text{max}}} \sum_{m=-\ell}^{+\ell} Y_{\ell m}^I(\hat{\mathbf{r}}) p_{\ell}^I(r) h_{\ell\ell}(Z_I) p_{\ell}^I(r') Y_{\ell m}^{I*}(\hat{\mathbf{r}}'), \quad (14)$$

with the normalized projector,

$$p_{\ell}^I(r) \propto \frac{r^{\ell} \exp[-r^2/2\beta_{\ell\ell}(Z_I)^2]}{\beta_{\ell\ell}(Z_I)^{\ell+3/2}}. \quad (15)$$

$h_{\ell\ell}(Z_I)$ and $\beta_{\ell\ell}(Z_I)$ are two adjustable atom-dependent parameters for each angular-momentum channel ℓ that are uniquely assigned to different atoms in the system according to the one-to-one mapping between Z_I and $\rho(\mathbf{R}_I)$ (Fig. 1). ACFs can be used as corrections to the approximate DFT functionals as suggested in Eq. (2). Therefore, even though the starting guess for the electron density in a self-consistent-field optimization may not have any cusps (thus no ACF corrections), after the first iteration, cusps at the atomic positions arise from the contribution of the approximate functional, $F^{\text{approx}}[\rho]$, with the consequent switching on of the ACF correction.

As an example, we will concentrate here on one particular category of ACFs that we have recently introduced to treat the lack of dispersion forces in DFT but the following argument is generally applicable. To gain insight into the physical meaning of the DCACP correction [Eq. (14)], we use the Funk-Hecke theorem (FHT) (Ref. 18) to derive the spherical harmonics coefficients of the atom-centered weighting functions, Γ_I and $\Delta\tilde{F}'(\mathbf{r}, \mathbf{r}')$, in Eq. (7).

The spherical harmonics expansion in Eq. (14) corresponds to a double convolution of the two-point quantity $\Delta\tilde{F}'$ with the one-point weighting functions Γ_I as in Eq. (7). According to the FHT (see Appendix), comparing Eq. (14)

with Eq. (A6), we find the following relation between the spherical harmonics coefficients of Γ_l , $\Delta\tilde{F}'$, and v_l^{ACF} :

$$p_\ell^l(r)h_{\ell\ell}p_\ell^l(r') = \frac{4\pi}{2\ell+1}\gamma_{\ell 0}^l(r)\Delta\tilde{f}'_{\ell 0}(r,r')\gamma_{\ell 0}^l(r'), \quad (16)$$

and, according to Eq. (A6), we can assign

$$\gamma_{\ell 0}^l(r) = \sqrt{h_{\ell\ell}} \frac{\exp[-r^2/2\beta_{\ell\ell}(Z_l)^2]}{\beta_{\ell\ell}(Z_l)^{\ell+3/2}}, \quad (17)$$

$$\Delta\tilde{f}'_{\ell 0}(r,r') = \frac{2\ell+1}{4\pi} r^\ell r'^\ell, \quad (18)$$

where we collect all atom-dependent terms into the definition of $\gamma_{\ell 0}^l$.

According to the definition of the functional correction in Eqs. (7) and (12), the atom-centered DCACP corrections are therefore generated by a weighted sum of “multiple moments,”

$$q_{\ell m}^i = \sqrt{\frac{2\ell+1}{4\pi}} \int d\mathbf{r} Y_{\ell m}(\hat{\mathbf{r}}) r^\ell \phi_i(\mathbf{r}). \quad (19)$$

In the DCACP approach, we have opted for a single-channel ($\ell=3$) expansion¹⁹ since we are mostly interested in the region around the van der Waals (vdW) minimum and less so in the long-range limit. In general, it gives excellent performance and transferability for vdW interactions up to ~ 5 Å but some deviations from the asymptotic dipolar nature^{20–23} are observed at long range. One channel is therefore sufficient to describe equilibrium properties very well and can be extended to several channels if required.

Since both the spherical harmonics (angular) and Gaussian function (radial) expansions adopted here form a complete set of orthonormal functions, they can, in principle, reproduce any function with arbitrary accuracy. It should thus be straightforward to achieve the r^{-6} behavior by including more projectors in the expansion. To demonstrate this, the H_2 dimer is chosen as an example; hydrogen is devoid of any nonlocal components in its atomic pseudopotential, and we are allowed to assign l as low as zero to the DCACP without any interference with the underlying atomic pseudopotential (the very different length scale also ensures minimal interference between the two). All DFT calculations have been carried out using the CPMD code,²⁴ the BLYP functional,^{25,26} Goedecker-Teter-Hutter pseudopotentials,¹⁷ and a plane-wave cutoff of 100 Ry in an isolated cell with dimensions $10 \times 10 \times 20$ Å³. Our implementation of $\Delta F[\rho]$ in the CPMD code²⁴ follows exactly the one for the nonlocal part of the separable nonlocal pseudopotentials.²⁷ (As in hybrid functionals, this introduces nonlocality in the DFT potential, which is no longer multiplicative. Improvements of the theory and its implementation can be achieved following the development of the optimized potential method, in which the DFT potential is derived using a chain rule for functional differentiation.) The hydrogen DCACP has been calibrated against a full configuration-interaction (CI) reference of H_2 dimer aligned in parallel,²⁸ using the scheme proposed in Ref. 12. The results are presented in Fig. 2. The “tail” of the

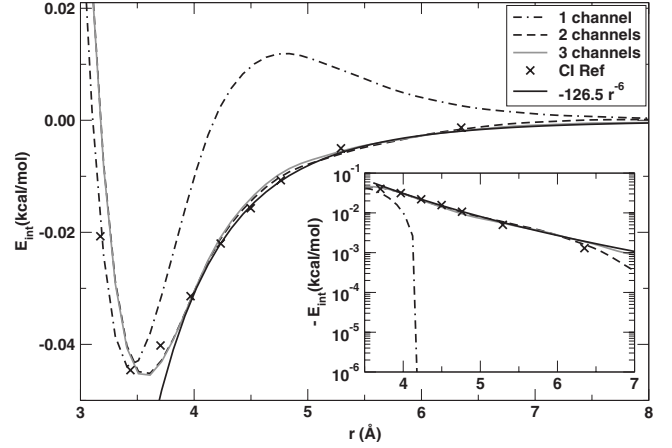


FIG. 2. Interaction energy of $(\text{H}_2)_2$ aligned in parallel computed with DCACPs having multiple projectors.

CI reference is fitted to a function of the form ar^{-6} and the two deviate slightly from each other, especially in the long-range limit, indicating the influence of higher order terms such as r^{-8} . In addition, a drastic improvement in the r^{-6} description is observed when the expansion of DCACPs includes more than one ℓ . Essentially, exact r^{-6} behavior can be reached by as few as two projectors. This clearly demonstrates that the DCACP approach is capable of reproducing the physically correct r^{-6} asymptotic limit even though this functional form is not explicitly imposed and that essentially arbitrarily accuracy with respect to high-level reference calculations can be obtained by using such a correction term.

To summarize, we have drawn on the atoms-in-molecules theory and the multicenter potential approach to show that it is possible to expand corrections to the approximated universal density functional in terms of multiatom-centered contributions. This expansion is unambiguously determined by the topology of the electron density: the cusp condition determines the centers of the expansion (the nuclear positions, R_I) and $\rho(R_I)$ determines the nature (Z_I) of the atom at that position. In this sense, this expansion can be considered universal, i.e., it depends solely on the electronic density. The final assessment of the multicenter functionals is obtained through a fitting procedure of the Z_I -dependent parameters used in $P_l(\mathbf{r}_l, \mathbf{r}'_l)$. This procedure, in principle, is carried out only once for each element, and it involves tuning the parameters so that the desired accuracy on any chosen molecular properties can be optimally reproduced. For the multicenter correction aimed to cure the lack of dispersion forces in DFT-GGA, we have shown that, with the example of $(\text{H}_2)_2$, it is possible to achieve the correct r^{-6} asymptotic tail in the interaction energy curve by including a sufficient number of components (as few as two) in the expansion in Eq. (14).

APPENDIX

We first introduce the decomposition of the spherical part of a one-point function $\Gamma(\mathbf{r})$ and a two-point function $F(\mathbf{r}, \mathbf{r}')$,

$$\Gamma(\mathbf{r}) = \sum_{l=0}^{\infty} \sum_{m=-l}^l \gamma_{lm}(r) Y_{lm}(\hat{\mathbf{r}}), \quad (A1)$$

$$F(\mathbf{r}, \mathbf{r}') = \sum_{l=0}^{\infty} \sum_{m=-l}^l \sum_{p=0}^{\infty} \sum_{q=-l}^p f_{lm,pq}(r, r') Y_{lm}^*(\hat{\mathbf{r}}) Y_{pq}(\hat{\mathbf{r}}'). \quad (\text{A2})$$

The convolution of these two functions in the first argument has the following expansion in spherical harmonics:

$$F \circ \Gamma(\mathbf{r}, \mathbf{r}') = \sum_{l=0}^{\infty} \sum_{m=-l}^l \sum_{p=0}^{\infty} \sum_{q=-l}^p (F \circ \Gamma)_{lm,pq}(r, r') Y_{lm}^*(\hat{\mathbf{r}}) Y_{pq}(\hat{\mathbf{r}}'), \quad (\text{A3})$$

with, according to the Funk-Hecke theorem,¹⁸ coefficients

$$(F \circ \Gamma)_{lm,pq}(r, r') = \sqrt{\frac{4\pi}{2l+1}} \gamma_{l0}(r) f_{lm,pq}(r, r'). \quad (\text{A4})$$

For the double convolution in Eq. (7) we finally get

$$(\Gamma \circ F \circ \Gamma)_{lm,pq}(r, r') = \frac{4\pi}{2l+1} \gamma_{l0}(r) f_{lm,pq}(r, r') \gamma_{l0}(r'). \quad (\text{A5})$$

In the case in which the matrix elements $f_{lm,pq}$ are diagonalizable, the spherical harmonics coefficients for the double convolution in Eq. (A5) become

$$(\Gamma \circ F \circ \Gamma)_{lm}(r, r') = \frac{4\pi}{2l+1} \gamma_{l0}(r) f_{lm}(r, r') \gamma_{l0}(r'), \quad (\text{A6})$$

and therefore

$$\Gamma \circ F \circ \Gamma(\mathbf{r}, \mathbf{r}') = \sum_{l=0}^{\infty} \sum_{m=-l}^l (\Gamma \circ F \circ \Gamma)_{lm}(r, r') Y_{lm}^*(\hat{\mathbf{r}}) Y_{lm}(\hat{\mathbf{r}}'). \quad (\text{A7})$$

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¹³Strictly speaking, the local maxima at the nuclear positions are not “true” (3,−3) critical points because the gradient vector of the charge density is discontinuous at the nuclear cusp that is present in both the wave function and the density. The critical point is labeled by its rank ω and signature σ in the form of (ω, σ) . The former is equal to the number of nonzero eigenvalues (of the Hessian matrix) of ρ at the critical point and the latter is the algebraic sum of the signs of the eigenvalues, i.e., (3, −3) denotes the critical point where all curvatures are negative and ρ is a local maximum (Ref. 10). Nevertheless, there always exists a function homeomorphic to $\rho(\mathbf{r}; \mathbf{R}_l)$ which coincides with ρ almost everywhere and for which the nuclear positions are (3,−3) critical points (Ref. 10). In this sense, the nuclear

positions behave topologically as do (3,−3) critical points in the charge distribution.

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