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Convergence of multipole expanded intermolecular interaction energies for Gaussian-type-function and Slater-type-function basis sets

Georg Jansen

Institut für Theoretische Chemie, Heinrich-Heine-Universität Düsseldorf, Universitätsstraße 1 40225 Düsseldorf, Germany
e-mail: georg@theochem.uni-duesseldorf.de

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Abstract. It is shown that the multipole expansion of each order of the polarization series converges for large enough intermolecular distances when finite basis sets of Gaussian or Slater-type functions are used to approximate molecular response properties. Convergence of the multipole expansion for each order of the polarization series does not imply convergence of the polarization series itself. A corresponding convergence condition is extracted from the general perturbation theory in a finite-dimensional space and is applied to the H + H^+ problem.

Key words: Polarization series – Gaussian-type and Slater-type functions – Elementary charge distributions – Overlap multipole moments

1 Introduction

A most important means for understanding and modeling intermolecular potential-energy surfaces is provided by the traditional multipole expansion for long-range interaction energies in combination with the so-called polarization series [1–3]. In polarization theory first the Hamiltonian of the "supermolecule" A + B is partitioned as

$$\hat{H} = \hat{H}^{\mathrm{A}} + \hat{H}^{\mathrm{B}} + \hat{V} \ , \tag{1}$$

where $\hat{H}^{\mathrm{A}}$ and $\hat{H}^{\mathrm{B}}$ are the Hamiltonians of the isolated molecules A and B, and $\hat{V}$ is the operator of the Coulombic interactions between the set $\mathscr{A}$ of all electrons and nuclei of system A with the set $\mathscr{B}$ of all electrons and nuclei of system B:

$$\hat{V} = \sum_{i\in\mathscr{A}} \sum_{j\in\mathscr{B}} \frac{q_i q_j}{|\mathbf{R} + \mathbf{r}_j - \mathbf{r}_i|} \ , \tag{2}$$

where $\mathbf{R}$ is the vector pointing from the origin of a local coordinate system for molecule A to that of B and $\mathbf{r}_i$ the position of a particle (electron or nucleus) with charge q_i relative to a molecular coordinate system. The electrons of system A are thus considered to be distinguishable from those of system B. Then a Rayleigh–Schrödinger perturbation series corresponding to Eq. (1) is constructed using products $|\psi_{\mathrm{a}}^{\mathrm{A}}\rangle|\psi_{\mathrm{b}}^{\mathrm{B}}\rangle$ of the unperturbed eigenstates of $\hat{H}^{\mathrm{A}}$ and $\hat{H}^{\mathrm{B}}$. For simplicity it will be assumed that $\hat{H}^{\mathrm{A}}$ and $\hat{H}^{\mathrm{B}}$ have nondegenerate ground states. The polarization energy of nth order is obtained as

$$E_{\mathrm{pol}}^{(n)} = \left\langle \Psi_0 | \hat{V} | \Psi_{\mathrm{pol}}^{(n-1)} \right\rangle \ , \tag{3}$$

with $|\Psi_{\mathrm{pol}}^{(0)}\rangle = |\Psi_0\rangle = |\psi_0^{\mathrm{A}}\rangle|\psi_0^{\mathrm{B}}\rangle$ and $E_{\mathrm{pol}}^{(0)} = E_0^{(0)} = E_0^{\mathrm{A}} + E_0^{\mathrm{B}}$. The polarization wavefunction of nth order is determined from the inhomogenous differential equation

$$(\hat{H}^{\mathrm{A}} + \hat{H}^{\mathrm{B}} - E_0)|\Psi_{\mathrm{pol}}^{(n)}\rangle = -\hat{V}|\Psi_{\mathrm{pol}}^{(n-1)}\rangle + \sum_{k=1}^{n} E_{\mathrm{pol}}^{(k)} |\Psi_{\mathrm{pol}}^{(n-k)}\rangle \tag{4}$$

in restricting its solution to the orthogonal complement of $|\Psi_0\rangle$. The multipole expansion of the different orders of the polarization series can now be introduced using a spherical tensor formulation [4] by substituting the Coulombic interaction operator, $\hat{V}$, with

$$\hat{V}_{\mathrm{mult}} = \lim_{L\to\infty} \sum_{\mathscr{L}=0}^{L} \sum_{M=-\mathscr{L}}^{\mathscr{L}} I_{\mathscr{L}M}(\mathbf{R}) \sum_{i\in\mathscr{A}} \sum_{j\in\mathscr{B}} q_i q_j R^*_{\mathscr{L}M}(\mathbf{r}_i - \mathbf{r}_j) \ , \tag{5}$$

where $R_{lm}(\mathbf{r})$ and $I_{lm}(\mathbf{r})$ denote regular and irregular spherical harmonics, respectively [4]. This series converges absolutely when all distances $|\mathbf{r}_i - \mathbf{r}_j|$ between the particles of the different subsystems are smaller than $R = |\mathbf{R}|$. On inserting the addition theorem

$$R^*_{\mathscr{L}M}(\mathbf{r}_i - \mathbf{r}_j) = \sum_{l=0}^{\mathscr{L}} \sum_{m=-l}^{l} \sum_{l'=0}^{\mathscr{L}} \sum_{m'=-l'}^{l'} \delta_{l+l',\mathscr{L}}$$

$$\times (-1)^{l'}\sqrt{\frac{(2\mathscr{L}+1)!}{(2l)!(2l')!}}\begin{pmatrix} l & l' & \mathscr{L} \\ m & m' & M \end{pmatrix} \times R_{lm}(\mathbf{r}_i)R_{l'm'}(\mathbf{r}_j) \ , \quad (6)$$

the resulting multipole expansion of the interaction operator converges to $\hat{V}$ when all particles of molecules A and B are found within nontouching spheres around the origins of the molecular coordinate systems.

Inserting the multipole expansion of the interaction operator into the polarization series leads to an expansion of the polarization energies and the total interaction energy in powers of $1/R$. The convergence properties of these $1/R$ expansions are not evident since the static and response charge densities of two molecules always overlap and the series (Eq. 5) does not converge when for at least one pair of particles $|\mathbf{r}_j - \mathbf{r}_i| > R$. The present knowledge of the convergence properties of $1/R$ expansions of interaction energies has been summarized in a recent review article by Jeziorsky et al. [3]:

> Theorem 1. The $1/R$ expansion of the total interaction energy converges asymptotically to the ground-state interaction energy [5, 6].
> Theorem 2. For each finite R, however, the $1/R$ expansion may diverge. Actual divergence of the series has been proven for the H_2 molecule [5] and the H_2^+ ion [6–8].
> Theorem 3. The $1/R$ expansion of the second-order polarization energy for the H_2^+ ion, i.e., its induction energy, diverges for all finite R [9].
> Theorem 4. The $1/R$ expansion of the second-order polarization energy for the H_2 molecule, i.e., its dispersion energy, diverges for all finite R [10].

In view of the fact that most electronic structure calculations are performed with finite-dimensional one-particle basis sets comprising a limited number of Gaussian-type functions (GTFs) or, sometimes, Slater-type functions (STFs) the following theorem due to Stone and Alderton [11, 12] and Vigné-Maeder and Claverie [13] is of particular interest:

> Theorem 5. Given that finite-dimensional GTF or STF basis sets are used to approximate each of the electronic charge densities of molecules A and B, the $1/R$ expansion of the first-order interaction energy
>
> $$E_{\mathrm{pol}}^{(1)} = \langle \psi_0^{\mathrm{A}}\psi_0^{\mathrm{B}}|\hat{V}|\psi_0^{\mathrm{A}}\psi_0^{\mathrm{B}}\rangle = \int \mathrm{d}\mathbf{r}\int \mathrm{d}\mathbf{r}'\frac{\rho^{\mathrm{A}}(\mathbf{r})\rho^{\mathrm{B}}(\mathbf{r}')}{|\mathbf{R}+\mathbf{r}'-\mathbf{r}|} \quad (7)$$
>
> converges, as long as the smallest spheres around the respective molecular origins which contain all nuclei and all centers of the basis functions do not touch.

Note that the $1/R$ expansion of $E_{\mathrm{pol}}^{(1)}$ is obtained from a formal replacement of $\hat{V}$ with $\hat{V}_{\mathrm{mult}}$, although the charge distributions and integrations in Eq. (7) extend to infinity. As a consequence, convergence of this $1/R$ expansion does not imply that it converges to $E_{\mathrm{pol}}^{(1)}$, but rather to some value different from it. Following the arguments given by Vigné-Maeder and Claverie [13] it is probable that the $1/R$ expansion of the first-order electrostatic energy converges in general, i.e., also for molecular charge distributions represented by complete basis sets. Yet this was not rigorously proven by the authors.

In practice not only the static electronic charge densities but also the molecular response properties, such as static and dynamic polarizabilities and hyperpolarizabilities, are calculated using finite-dimensional basis sets; therefore, it is interesting to see whether a theorem analogous to theorem 5 holds for second- and higher-order contributions to the intermolecular interaction energy in these cases. As shown in the following theorem 5 can indeed be generalized to

> Theorem 6. Given that a finite number of GTFs or STFs is used as a one-particle basis set, the multipole expansion of each order of the polarization series converges, as long as the smallest spheres around the respective molecular origins which contain all nuclei and all centers of the basis functions do not touch.

This does not imply, however, convergence of the multipole expanded polarization series itself. In Sect. 4 a sufficient condition for convergence of the multipole expanded polarization series is extracted from the general perturbation theory in a finite-dimensional space [14, 15], and numerical illustrations are given for the simplest possible case, i.e., for the hydrogen atom represented in a GTF basis set which is perturbed by a proton.

2 Multipole expansions of elementary charge distributions

While numerical techniques can be employed for electronic structure calculations on atoms and linear molecules, nearly all calculations on polyatomic molecules are carried out using spin-orbital basis sets $\langle \mathbf{r}\omega|\mathrm{a}\rangle = \phi_{\mathrm{a}}(\mathbf{r}\omega) = \chi_{\mathrm{a}}(\mathbf{r})\omega_{\mathrm{a}}$ derived from a finite number, N, of spatial basis functions, $\chi_{\mathrm{a}}(\mathbf{r})$, multiplied by spin-up and spin-down functions, ω_{a}. The electronic charge density, $\rho_{\mathrm{el}}(\mathbf{r})$, can then be expressed in terms of elementary charge distributions (ECDs), i.e., all possible products $\chi_{\mathrm{a}}^*\chi_{\mathrm{b}}$ of the spatial basis functions. Thus, the electron–electron interaction part of $E_{\mathrm{pol}}^{(1)}$ will be a superposition of the Coulombic interactions between ECDs:

$$\begin{aligned}\int \mathrm{d}\mathbf{r}\int \mathrm{d}\mathbf{r}'\frac{\rho_{\mathrm{el}}^{\mathrm{A}}(\mathbf{r})\rho_{\mathrm{el}}^{\mathrm{B}}(\mathbf{r}')}{|\mathbf{R}+\mathbf{r}'-\mathbf{r}|} &= \sum_{\mathrm{a,b}}\sum_{\mathrm{c,d}} P_{\mathrm{ab}}^{\mathrm{A}}P_{\mathrm{cd}}^{\mathrm{B}}\int \mathrm{d}\mathbf{r}\int \mathrm{d}\mathbf{r}'\frac{\chi_{\mathrm{a}}^*(\mathbf{r})\chi_{\mathrm{c}}^*(\mathbf{r}')\chi_{\mathrm{b}}(\mathbf{r})\chi_{\mathrm{d}}(\mathbf{r}')}{|\mathbf{R}+\mathbf{r}'-\mathbf{r}|} \\ &= \sum_{\mathrm{a,b}}\sum_{\mathrm{c,d}} P_{\mathrm{ab}}^{\mathrm{A}}P_{\mathrm{cd}}^{\mathrm{B}}\langle \mathrm{ac}|\mathrm{bd}\rangle \ . \end{aligned} \quad (8)$$

Suppose that the spatial basis function set is composed of (complex) spherical GTFs

$$\chi_{\mathrm{a}}(\mathbf{r}) = G_{n_{\mathrm{a}}l_{\mathrm{a}}m_{\mathrm{a}}}(\alpha_{\mathrm{a}},\mathbf{r}_{\mathrm{a}}) = R_{l_{\mathrm{a}}m_{\mathrm{a}}}(\mathbf{r}_{\mathrm{a}})\partial_{-\alpha_{\mathrm{a}}}^{k_{\mathrm{a}}}\mathrm{e}^{-\alpha_{\mathrm{a}}\mathbf{r}_{\mathrm{a}}^2}; \quad n_{\mathrm{a}} = l_{\mathrm{a}} + 2k_{\mathrm{a}} \ , \quad (9)$$

or of spherical STFs

$$\chi_a(\mathbf{r}) = S_{n_a l_a m_a}(\alpha_a, \mathbf{r}_a) = R_{l_a m_a}(\mathbf{r}_a)\partial^{k_a}_{-\alpha_a} e^{-\alpha_a r_a}; \quad n_a = l_a + k_a \ , \quad (10)$$

where $\mathbf{r}_a = \mathbf{r} - \mathbf{R}_a$ is the distance vector to the center $\mathbf{R}_a$ of the basis function ($r_a = |\mathbf{r}_a|$), α_a its (positive) exponent, and $\partial^{k_a}_{-\alpha_a}$ means the k_ath derivative with respect to $(-\alpha_a)$. It is easy to see that the Coulombic interaction between two ECDs has a multipole expansion consisting of a finite number of terms when

1. The GTFs or STFs contributing to the first ECD $\chi^*_a\chi_b$ are localized on the same center $\mathbf{R}_a = \mathbf{R}_b$.
2. The GTFs or STFs contributing to the second ECD $\chi^*_c\chi_d$ are localized on the same center $\mathbf{R}_c = \mathbf{R}_d$.
3. The multipole expansion centers coincide with $\mathbf{R}_a$ and $\mathbf{R}_c$.

This follows from integration over the angular part, Ω_a, of the spherical coordinates of $\mathbf{r}_a$,

$$\int d\Omega_a R^*_{l_a m_a}(\mathbf{r}_a) R_{lm}(\mathbf{r}_a) R_{l_b m_b}(\mathbf{r}_a) = r_a^{l_a+l_b+l}(-1)^m 4\pi \begin{pmatrix} l_a & l_b & l \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_a & l_b & l \\ -m_a & m_b & m \end{pmatrix} , \quad (11)$$

which vanishes for $l > l_a + l_b$ [16], and an analogous relation for the integral over Ω_c.

In the case of GTFs a similar statement holds for ECDs for which $\mathbf{R}_a \neq \mathbf{R}_b$ and/or $\mathbf{R}_c \neq \mathbf{R}_d$. This was first observed by Hall and Martin [17, 18] and is a direct consequence of the Gaussian product theorem [19]

$$e^{-\alpha_a \mathbf{r}_a^2} e^{-\alpha_b \mathbf{r}_b^2} = e^{-\frac{\alpha_a\alpha_b}{\alpha_a+\alpha_b}(\mathbf{R}_a-\mathbf{R}_b)^2} e^{-(\alpha_a+\alpha_b)\mathbf{r}_{ab}^2} \ , \quad (12)$$

$$\mathbf{r}_{ab} = \mathbf{r} - \mathbf{R}_{ab} = \mathbf{r} - (\alpha_a\mathbf{R}_a + \alpha_b\mathbf{R}_b)/(\alpha_a + \alpha_b) \ , \quad (13)$$

which states that a product of two 1s GTFs ($n = l = m = 0$) centered around $\mathbf{R}_a$ and $\mathbf{R}_b$, respectively, is proportional to a single 1s GTF centered around the "overlap center" $\mathbf{R}_{ab}$, i.e., a point on the line between $\mathbf{R}_a$ and $\mathbf{R}_b$. For a product of a 1s GTF with, say, a 3s GTF ($n = 2$, $l = m = 0$, note from Eq. (9) that 2s GTFs normally are not employed) application of $\partial^1_{-\alpha}$ shows that one will obtain a linear combination of a 1s and a 3s GTF, both with exponent $(\alpha_a + \alpha_b)$ and both centered around $\mathbf{R}_{ab}$. This can easily be extended to products of s GTFs with higher n quantum numbers as well. Furthermore, the product of a 1s GTF with, say, a 3d GTF is equivalent to a linear combination of 1s, 2p, and 3d GTFs, all three centered around $\mathbf{R}_{ab}$ and with exponent $(\alpha_a + \alpha_b)$. This follows from the addition theorem (Eq. 6) for $R_{3m}(\mathbf{r}_b) = R_{3m}(\mathbf{r}_{ab} - \mathbf{R}_b + \mathbf{R}_{ab})$. In a similar way one can see that every product of two GTFs located at $\mathbf{R}_a$ and $\mathbf{R}_b$ with exponents α_a and α_b and angular momentum quantum numbers l_a and l_b, respectively, is equivalent to a finite linear combination of GTFs with angular momenta of at most $(l_a + l_b)$, all having the same exponent $(\alpha_a + \alpha_b)$ and all located at the overlap center $\mathbf{R}_{ab}$. Choosing $\mathbf{R}_{ab}$ and the corresponding overlap center $\mathbf{R}_{cd}$ of the second ECD as the expansion centers, it is again found that the multipole series for interaction of two ECDs terminates at $L = l_a + l_b + l_c + l_d$.

Let us denominate the interaction energy between these "overlap multipole moments" (OMMs) by $W^{ac,bd}_{OMM}$. Please remember that $W^{ac,bd}_{OMM} \neq \langle ac|bd\rangle$ since it results from a formal replacement of $1/|\mathbf{R} + \mathbf{r}' - \mathbf{r}| = 1/|(\mathbf{R} + \mathbf{R}_{ab} - \mathbf{R}_{cd}) + \mathbf{r}'_{cd} - \mathbf{r}_{ab}|$ with a multipole expansion analogous to Eqs. (5) and (6) in $\mathbf{r}_{ab}$ and $\mathbf{r}'_{cd}$ which is not valid for $|\mathbf{r}'_{cd} - \mathbf{r}_{ab}| > |\mathbf{R} + \mathbf{R}_{ab} - \mathbf{R}_{cd}|$. Nevertheless, $W^{ac,bd}_{OMM}$ is a finite number which represents the exact multipolar part of the Coulombic interaction energy $\langle ac|bd\rangle$.

In contrast to the situation for GTFs, an ECD composed of two STFs which are located at different centers cannot be reduced to a finite linear combination of STFs. As a consequence, there is no center such as the overlap center for GTFs which would guarantee a terminating multipole expansion. Yet, the integral transformation

$$e^{-\alpha_a r_a} = \int_0^\infty ds_a \frac{\alpha_a e^{-\alpha_a^2/4s_a}}{2\sqrt{\pi}\ s_a^{3/2}} e^{-s_a \mathbf{r}_a^2} \quad (14)$$

between STFs and GTFs [20, 21] has been used by Vigné-Maeder and Claverie [13] to point out that the multipolar part of an ECD composed of two 1s STFs can be reduced to a charged line between the two STF centers. Pursuing this idea it is not difficult to see that

$$e^{-\alpha_a r_a} e^{-\alpha_b r_b} = \int_0^1 du \int_0^\infty d\beta\, \beta F_{ab}(\beta, u) e^{-\beta r_u^2} \ , \quad (15)$$

where

$$F_{ab}(\beta,u) = \frac{\alpha_a\alpha_b}{4\pi} \frac{\exp\left\{-\left[(1-u)\alpha_a^2 + u\alpha_b^2\right]/[4u(1-u)\beta] - u(1-u)\beta(\mathbf{R}_a - \mathbf{R}_b)^2\right\}}{\beta^3 u^{3/2}(1-u)^{3/2}} \quad (16)$$

and

$$\mathbf{r}_u = \mathbf{r} - \mathbf{R}_u = \mathbf{r} - [u\mathbf{R}_a + (1-u)\mathbf{R}_b] \ , \quad (17)$$

$\mathbf{R}_u$ being is a point on the line between $\mathbf{R}_a$ and $\mathbf{R}_b$. Inserting Eq. (15) and a corresponding expression for the second ECD into the two-electron integral $\langle ac|bd\rangle$, replacing $1/|\mathbf{R} + \mathbf{r}' - \mathbf{r}| = 1/|(\mathbf{R} + \mathbf{R}_v - \mathbf{R}_u) + \mathbf{r}'_v - \mathbf{r}_u|$ with a multipole expansion analogous to Eqs. (5) and (6) in $\mathbf{r}'_v$ and $\mathbf{r}_u$, and performing the integrations over these variables yields

$$W^{ac,bd}_{OMM} = \int_0^1 du \int_0^1 dv\, q_{ab}(u) q_{ab}(v) I_{00}(\mathbf{R} + \mathbf{R}_v - \mathbf{R}_u) \ , \quad (18)$$

where

$$q_{ab}(u) = \int_0^\infty d\beta\, \beta F_{ab}(\beta,u) \int d\mathbf{r}_u\, R_{00}(\mathbf{r}_u) e^{-\beta \mathbf{r}_u^2} = \pi^{3/2} \int_0^\infty d\beta\, F_{ab}(\beta,u) \Big/ \sqrt{\beta} \ . \quad (19)$$

These formulae show that the exact multipolar part of $\langle ac|bd\rangle$ is given by the Coulombic interaction between continuous charge distributions $q_{ab}(u)$ and $q_{cd}(v)$ located on the lines $\mathbf{R}_u$ and $\mathbf{R}_v$, respectively. In analogy to the situation for GTFs, this exact multipolar part will also be called $W_{OMM}^{ac,bd}$. Furthermore, following similar considerations one can see that the product of a 1s STF with a 2p STF has an exact multipolar part consisting of continuous charge and dipole distributions spread along the line between their centers, that the product of two 2p STFs leads to charge, dipole and quadrupole distributions, and so on. Finally, note that the same is also true for products of STFs with higher n quantum numbers (2s, 3s, 3p,...) since, for example, $\partial^{k_a}_{-\alpha_a} q_{ab}(u)$ is also a continuous charge distribution along $\mathbf{R}_u$.

Consider now the situation when the multipole expansion for the interaction of two ECDs is performed around the origins of the molecular coordinate systems instead of the overlap centers for GTFs or the "overlap lines" for STFs. If the molecular origin does not coincide with an overlap center, there will be no highest nonvanishing multipole moment. Thus, the energy of interaction $W_{1/R^L}^{ac,bd}$ of the multipoles at the molecular origin will not be constant after a certain power L of $1/R$. Yet, if the point and line multipolar distributions contributing to the exact multipolar part, $W_{OMM}^{ac,bd}$, of $\langle ac|bd\rangle$ are located within spheres of radius ϱ_a and ϱ_b around the respective molecular origins and if these spheres do not touch ($\varrho_a + \varrho_b < R$) it follows from the uniform convergence of Eqs. (5) and (6) under these circumstances that

$$\lim_{L\to\infty} W_{1/R^L}^{ac,bd} = W_{OMM}^{ac,bd} \ . \tag{20}$$

The interaction between the multipoles equivalent to the ECDs of molecule A and the nuclear point charges of molecule B (denoted by $W_{OMM}^{ab,B}$) and vice versa can be treated as a special case of the above considerations. Furthermore, generalization to (finite) linear combinations of the spherical GTFs or STFs such as Cartesian, real spherical or contracted basis functions is straightforward. Theorem 5 then follows directly from Eq. (20) and the fact that there is only a finite number of ECDs which contributes to the electronic charge distributions.

3 Convergence of multipole expanded polarization energies

In order to extend theorem 5 to higher-order polarization energies and wavefunctions we first remember that the true eigenstates of the unperturbed molecular Hamiltonians are usually not available. In general, the best one can hope for is their approximation by full configuration interaction (CI) wavefunctions constructed from the finite-dimensional one-particle basis set. Using the same one-particle basis set for the evaluation of all of its terms the polarization series results from perturbation theory in a finite-dimensional space, as treated in chapter 2 of Kato's book [14] or, even more extensively, in Baumgärtel's book [15]. This finite- (though, in general, high-) dimensional space is spanned by all products $|\Phi_r\rangle = |\phi_a^A\rangle|\phi_b^B\rangle$ of the full CI wavefunctions $|\phi_a^A\rangle$ and $|\phi_b^B\rangle$ for molecules A and B, respectively. These wavefunctions can be represented as eigenstates of a second-quantized molecular Hamiltonian, which in the general case of a nonorthogonal one-particle basis set can conveniently be written as [22]

$$\mathscr{H}^A = (S_A^{-1})_{ab}\langle b|\hat{h}^A|c\rangle a_a^+ \tilde{a}_c^- + \frac{1}{2}(S_A^{-1})_{ab}(S_A^{-1})_{cd}\langle bd|ef\rangle a_a^+ a_c^+ \tilde{a}_f^- \tilde{a}_e^- + W_{nuc}^A \ . \tag{21}$$

The creation operator of a spin orbital, χ_a, is denoted by a_a^+, the annihilation operator of the corresponding biorthogonal orbital by $\tilde{a}_a^-$, $(S_A^{-1})_{ab}$ is an element of the inverse of the overlap matrix, and W_{nuc}^A stands for the nuclear interaction energy of the molecule. The summation convention was employed in Eq. (21) and will also be used in the following. A completely analogous equation holds for molecule B, however with all a_a^+ replaced by b_a^+ and all $\tilde{a}_a^-$ by $\tilde{b}_a^-$. The distinction between a_a^+ and b_a^+ is crucial for polarization theory owing to the underlying assumption of distinguishability between the electrons in molecules A and B, respectively. The operator of the intermolecular interaction potential can now be written as

$$\mathscr{V} = (S_A^{-1})_{ab}\langle b|\hat{V}_{nuc}^B|c\rangle a_a^+ \tilde{a}_c^- + (S_B^{-1})_{de}\langle e|\hat{V}_{nuc}^A|f\rangle b_d^+ \tilde{b}_f^- + (S_A^{-1})_{ab}(S_B^{-1})_{de}\langle be|cf\rangle a_a^+ \tilde{a}_c^- b_d^+ \tilde{b}_f^- + W_{nuc}^{AB} \ . \tag{22}$$

$\hat{V}_{nuc}^A$ denotes the operator of the electric potential of the nuclei of molecule A, W_{nuc}^{AB} the electrostatic interaction energy between the nuclei of both molecules. A second-quantized interaction operator for indistinguishable electrons was given by Mayer (the sum of the Hamiltonians $\hat{H}_2$ and $\hat{H}_3$ of Ref. [23]).

Replacing the one- and two-electron integrals by their exact multipolar parts one can define an exact multipolar intermolecular interaction operator in a similar way as was done in Refs. [11–13] for the exact multipolar part of a molecular charge distribution:

$$\mathscr{V}_{OMM} = (S_A^{-1})_{ab} W_{OMM}^{bc,B} a_a^+ \tilde{a}_c^- + (S_B^{-1})_{de} W_{OMM}^{ef,A} b_d^+ \tilde{b}_f^- + (S_A^{-1})_{ab}(S_B^{-1})_{de} W_{OMM}^{bc,ef} a_a^+ \tilde{a}_c^- b_d^+ \tilde{b}_f^- + W_{nuc}^{AB} \ . \tag{23}$$

Since the operator (Eq. 23) contains only a finite number of terms it is trivially a bound operator when finite-dimensional molecule centered basis sets are used and when the envelopes of the two molecules containing the nuclei and all centers of the GTFs or STFs and the straight lines connecting them do not touch. Replacing $\mathscr{V}$ by $\mathscr{V}_{OMM}$ in the finite-dimensional analogs to Eqs. (3) and (4) defines an exact (for the given basis set) multipolar polarization series

$$E_{OMM}^{(n)} = \left\langle \Phi_0 | \mathscr{V}_{OMM} | \Phi_{OMM}^{(n-1)} \right\rangle \ , \tag{24}$$

$$|\Phi_{OMM}^{(n)}\rangle = \mathscr{R}_0 \left(-\mathscr{V}_{OMM}|\Phi_{OMM}^{(n-1)}\rangle + \sum_{k=1}^{n} E_{OMM}^{(k)} |\Phi_{OMM}^{(n-k)}\rangle \right) \ , \tag{25}$$

where

$$\mathscr{R}_0 = \sum_{r\neq 0} \frac{|\Phi_r^{(0)}\rangle\langle\Phi_r^{(0)}|}{E_r^{(0)} - E_0^{(0)}} \tag{26}$$

is the reduced resolvent of the ground state of $\mathscr{H}^{\mathrm{A}} + \mathscr{H}^{\mathrm{B}}$.

On the other hand, an ordinary multipole expanded polarization series including terms of a power in $1/R$ up to $1/R^L$ is obtained by replacing $\mathscr{V}$ with an operator $\mathscr{V}_{1/R^L}$, which is defined in analogy to $\mathscr{V}_{\mathrm{OMM}}$ using the matrix elements W_{1/R^L} instead of W_{OMM}. Using $\|\hat{O}\| = \sup_{\varphi,\varphi'\neq 0} |\langle\varphi|\hat{O}|\varphi'\rangle|/(\|\varphi\|\|\varphi'\|)$ it is easy to see that under the operator norm

$$\lim_{L\to\infty} \|\mathscr{V}_{1/R^L} - \mathscr{V}_{\mathrm{OMM}}\| = 0 \ , \tag{27}$$

since for each φ and φ' the expectation value $\langle\varphi|\mathscr{V}_{1/R^L}|\varphi'\rangle$ is just a finite sum of terms converging towards $\langle\varphi|\mathscr{V}_{\mathrm{OMM}}|\varphi'\rangle$. As a special case it follows from Eq. (3) that $E^{(1)}_{1/R^L} \to E^{(1)}_{\mathrm{OMM}}$, as is already known from the last section. Furthermore, one has

$$\begin{aligned}\|\phi^{(1)}_{1/R^L} - \phi^{(1)}_{\mathrm{OMM}}\| &= \|\mathscr{R}_0(\mathscr{V}_{1/R^L} - \mathscr{V}_{\mathrm{OMM}})\phi_0\| \\ &\leq \|\mathscr{R}_0\|\|\mathscr{V}_{1/R^L} - \mathscr{V}_{\mathrm{OMM}}\| \ ,\end{aligned} \tag{28}$$

so that $\lim_{L\to\infty} \Phi^{(1)}_{1/R^L} = \Phi^{(1)}_{\mathrm{OMM}}$, and theorem 6 is seen to hold for the first-order wavefunction as well. For higher orders in n complete induction can be used to show theorem 6. Observe that

$$\begin{aligned}&\|\mathscr{V}_{1/R^L}\Phi^{(n-1)}_{1/R^L} - \mathscr{V}_{\mathrm{OMM}}\Phi^{(n-1)}_{\mathrm{OMM}}\| \\ &\quad\leq \|\mathscr{V}_{1/R^L} - \mathscr{V}_{\mathrm{OMM}}\|\|\Phi^{(n-1)}_{\mathrm{OMM}}\| \\ &\qquad + \|\mathscr{V}_{\mathrm{OMM}}\|\|\Phi^{(n-1)}_{1/R^L} - \Phi^{(n-1)}_{\mathrm{OMM}}\| \\ &\qquad + \|\mathscr{V}_{1/R^L} - \mathscr{V}_{\mathrm{OMM}}\|\|\Phi^{(n-1)}_{1/R^L} - \Phi^{(n-1)}_{\mathrm{OMM}}\|\end{aligned} \tag{29}$$

and, therefore, $\mathscr{V}_{1/R^L}\Phi^{(n-1)}_{1/R^L} \to \mathscr{V}_{\mathrm{OMM}}\Phi^{(n-1)}_{\mathrm{OMM}}$ when $\Phi^{(n-1)}_{1/R^L} \to \Phi^{(n-1)}_{\mathrm{OMM}}$. In an analogous manner one finds $E^{(k)}_{1/R^L}\Phi^{(n-k)}_{1/R^L} \to E^{(k)}_{\mathrm{OMM}}\Phi^{(n-k)}_{\mathrm{OMM}}$. Utilizing this with the recursive Eqs. (24) and (25) and their counterparts expanded in $1/R^L$ proves theorem 6 for the higher-order corrections.

4 Convergence of the multipole expanded polarization series

Convergence of the $1/R$ expansion with increasing powers of L for each individual nth-order term of the polarization series, however, has to be clearly distinguished from convergence of the multipole-expanded polarization series itself, i.e., with increasing order n. Its convergence is only guaranteed when $a_0 = \min_\alpha \|\mathscr{V}_{\mathrm{OMM}} - \alpha\|$ is smaller than $(E_1^{(0)} - E_0^{(0)})/2$, where α is a scalar [24]. Since $\mathscr{V}_{\mathrm{OMM}}$ is a hermitian operator it can be diagonalized in the product space of the full CI wavefunctions to yield eigenvalues between a lowest, $U^{\mathrm{low}}_{\mathrm{OMM}}$, and a highest, $U^{\mathrm{high}}_{\mathrm{OMM}}$, eigenvalue. Because of $\|\mathscr{V}_{\mathrm{OMM}} - \alpha\| = \max(|U^{\mathrm{low}}_{\mathrm{OMM}} - \alpha|, |U^{\mathrm{high}}_{\mathrm{OMM}} - \alpha|)$ one finds $a_0 = (U^{\mathrm{high}}_{\mathrm{OMM}} - U^{\mathrm{low}}_{\mathrm{OMM}})/2$. A sufficient condition for convergence of the polarization series with the OMM interaction operator $\mathscr{V}_{\mathrm{OMM}}$ is therefore,

$$U^{\mathrm{high}}_{\mathrm{OMM}} - U^{\mathrm{low}}_{\mathrm{OMM}} < E_1^{(0)} - E_0^{(0)} \ , \tag{30}$$

where $E_1^{(0)} - E_0^{(0)}$ is the lower of the first excitation energies of the isolated molecules A and B. Inserting this into the "best possible" estimate of Kato [25] yields

$$\begin{aligned}|E^{(n)}_{\mathrm{OMM}}| \leq \min(1, N/n)\frac{\Gamma[(n-1)/2]}{\sqrt{\pi}\Gamma(n/2)}\frac{U^{\mathrm{high}}_{\mathrm{OMM}} - U^{\mathrm{low}}_{\mathrm{OMM}}}{4} \\ \times \left(\frac{U^{\mathrm{high}}_{\mathrm{OMM}} - U^{\mathrm{low}}_{\mathrm{OMM}}}{E_1^{(0)} - E_0^{(0)}}\right)^{n-1} \quad \text{for } n \geq 2 \ ,\end{aligned} \tag{31}$$

where N is the product of the dimensions of the full CI spaces for molecules A and B, and $\Gamma(x)$ is the gamma function. Note that an entirely analogous convergence criterion holds if the OMM interaction operator, $\mathscr{V}_{\mathrm{OMM}}$, is replaced by its $1/R$-expanded approximation, $\mathscr{V}_{1/R^L}$, with some finite L, and that in this case $U^{\mathrm{high}}_{\mathrm{OMM}}$ and $U^{\mathrm{low}}_{\mathrm{OMM}}$ have to be substituted by $U^{\mathrm{high}}_{1/R^L}$ and U^{low}_{1/R^L}.

This convergence criterion and Eq. (31) are not very helpful in practical calculations, since in general the product space spanned by all molecular full CI wavefunctions will be much too large to calculate the OMM or $1/R^L$ interaction matrices. Nevertheless, it is interesting to apply Eqs. (30) and (31) to the simplest possible case, the hydrogen atom in a GTF basis set representation which is perturbed by a proton at some fixed internuclear distance, R. In this case (as in all cases involving only atoms) there is no difference between the OMM and the $1/R$-expanded interaction operator when the nuclei are chosen as expansion centers and L is large enough. Let us define a radius of convergence, $R^{\mathrm{est}}_{\mathrm{conv}}$, belonging to Kato's estimate as that internuclear distance where $U^{\mathrm{high}}_{\mathrm{OMM}} - U^{\mathrm{low}}_{\mathrm{OMM}} = E_1^{(0)} - E_0^{(0)}$. The polarization series must converge for $R > R^{\mathrm{est}}_{\mathrm{conv}}$. Table 1 contains a comparison of $R^{\mathrm{est}}_{\mathrm{conv}}$ and the convergence radius, $R^{(100)}_{\mathrm{conv}}$, defined as the smallest internuclear distance (varied in steps of 0.05 bohr) where the polarization energy summed to order $n = 100$ was found to deviate at most within numerical limits from the "infinite-order" result, $E_{\mathrm{OMM}}(R)$, which is obtained from diagonalization of the total Hamiltonian matrix, $\mathscr{H}^{\mathrm{H}} + \mathscr{V}_{\mathrm{OMM}}$. The infinite-, second-, and third-order results for an internuclear separation of 5.0 bohr are also shown in Table 1; the corresponding estimates due to Eq. (31) are given in parentheses. The labels DZP, TZ2P, and TZ + 2P denote the hydrogen-atom basis sets of the 6-31G**, 6-311G(2d,2p), and 6-311 + + G(2d,2p) basis sets in the GAUSSIAN library [26], the labels Pol-3s2p and ANO-6s4p3d denote Sadlej's polarization and Widmark's atomic natural orbital contracted basis sets in the MOLCAS library [27]. The other, nonstandard, basis sets were derived from Duijneveldt's uncontracted seven 1s GTFs set [28]: 7s5p3d1f denotes a basis set where five 2p, three 3d, and one 4f GTF with the same exponents as the most diffuse 1s GTFs have been added. To these, one or two diffuse functions of each type with exponents 0.027962 and 0.009787 were added to yield the 8s6p4d2f and 9s7p5d3f sets. The remaining smaller basis sets were obtained by deleting the 4f and 3d GTFs from these.

Table 1. Convergence radii, R_{conv} (Bohr), and polarization energies, E (Hartree), at $R = 5$ bohr for $H + H^+$. For an explanation of the basis sets see text

Basis	$R_{\mathrm{conv}}^{\mathrm{est}}$	$R_{\mathrm{conv}}^{(100)}$	$-E_{\mathrm{OMM}}$	$-E_{\mathrm{OMM}}^{(2)}$	$-E_{\mathrm{OMM}}^{(3)}$
DZP	1.098	0.85	2.0607×10^{-4}	2.0574×10^{-4} (4.8918×10^{-4})	3.5084×10^{-7} (1.4066×10^{-5})
TZ2P	2.107	1.75	1.5880×10^{-3}	1.5675×10^{-3} (3.7610×10^{-3})	2.2352×10^{-5} (4.0504×10^{-4})
TZ + 2P	2.468	1.75	1.5864×10^{-3}	1.5658×10^{-3} (5.3022×10^{-3})	2.2327×10^{-5} (7.9636×10^{-4})
Pol-3s2p	3.509	3.05	3.9544×10^{-3}	3.5896×10^{-3} (2.1247×10^{-2})	2.7694×10^{-4} (6.4051×10^{-3})
ANO-6s4p3d	4.034	3.35	4.3644×10^{-3}	3.7686×10^{-3} (3.6223×10^{-2})	4.3094×10^{-4} (1.4298×10^{-2})
7s5p	3.837	3.30	3.9959×10^{-3}	3.5917×10^{-3} (3.1400×10^{-2})	2.9406×10^{-4} (1.1270×10^{-2})
8s6p	5.247	4.60	4.1312×10^{-3}	3.6015×10^{-3} (1.2108×10^{-1})	3.0673×10^{-4} (8.7583×10^{-2})
9s7p	7.272	6.25	2.6962×10^{-1}	3.6012×10^{-3} (7.4219×10^{-1})	3.0715×10^{-4} (1.3294)
7s5p3d	5.165	4.55	6.1380×10^{-3}	4.0653×10^{-3} (1.1810×10^{-1})	8.9046×10^{-4} (8.2212×10^{-2})
8s6p4d	7.359	6.80	7.2840×10^{-1}	4.0810×10^{-3} (1.8184)	9.5122×10^{-4} (5.0970)
9s7p5d	10.636	9.80	6.5656	4.0813×10^{-3} (7.8406×10)	9.6069×10^{-4} (1.4435×10^{3})
7s5p3d1f	5.906	5.25	2.4740×10^{-2}	4.2208×10^{-3} (3.0149×10^{-1})	1.3337×10^{-3} (3.3532×10^{-1})
8s6p4d2f	8.803	8.20	5.0317	4.2410×10^{-3} (4.6735×10)	1.4928×10^{-3} (6.6412×10^{2})
9s7p5d3f	13.157	12.45	1.0186×10^{2}	4.2456×10^{-3} (1.9810×10^{4})	2.1763×10^{-3} (5.7973×10^{6})

The first observation following from Table 1 is that $R_{\mathrm{conv}}^{\mathrm{est}}$ provides a very reasonable estimate for the smallest internuclear distance where the polarization series in a multipolar approximation still converges: the radius for which the polarization energies summed to $n = 100$ start to deviate appreciably from the infinite-order result is only 0.2–1.1 bohr smaller. As expected, augmenting the basis set with diffuse and high angular momentum basis functions leads to an increase in the radius for which the multipole expanded polarization series diverges. The main effect of these functions is to push the lowest and highest eigenvalues of the OMM interaction matrix apart, once the s and p function sets are sufficiently large to yield reasonable $1s \rightarrow 2s$ or $1s \rightarrow 2p$ excitation energies.

An exception is seen when comparing the results for the TZ2P and TZ + 2P basis sets, which differ only in a single diffuse s function. Here the first excitation energy of 0.526 hartree as obtained with the TZ2P basis set compares very badly to the exact value of 0.375 hartree for the $1s \rightarrow 2s$ and $1s \rightarrow 2p$ transitions, while the value of 0.381 for the TZ + 2P basis set is much more reasonable. At the same time $U_{\mathrm{OMM}}^{\mathrm{high}} - U_{\mathrm{OMM}}^{\mathrm{low}}$ is hardly affected (0.889 versus 0.899 hartree, at $R = 5$ bohr), thus explaining the change in $R_{\mathrm{conv}}^{\mathrm{est}}$. In contrast $R_{\mathrm{conv}}^{(100)}$ remains practically unaltered since the first excitation energies for these basis sets correspond to $1s \rightarrow 2s$ excitations with zero transition matrix elements. A way to improve the estimates for the first five basis sets listed in Table 1, which all have insufficient p function sets, would be to use the energy of the first multipole-allowed transition, i.e., $1s \rightarrow 2p$ in Eq. (30) instead of blindly using $E_1^{(0)}$. Doing so brings $R_{\mathrm{conv}}^{\mathrm{est}}$ down to 0.760 (DZP), 1.751 (TZ2P), 1.758 (TZ + 2P), 3.378 (Pol-3s2p), and 3.891 bohr (ANO-6s4p3d). For the DZP basis set this is even smaller than $R_{\mathrm{conv}}^{(100)}$, showing that the polarization series will converge much later than at $n = 100$ for this very small distance of only 0.76 bohr. For all other basis sets the $1s \rightarrow 2p$ excitation energy was found to be the lowest excitation energy, so nothing would change here.

Using the $1s \rightarrow 2p$ transition energy in Eq. (31) also leads to improved estimates for the polarization energies of different orders: in the case of the DZP basis set and an internuclear separation of 5.0 bohr one has $|E_{\mathrm{OMM}}^{(2)}| \leq 2.2003 \times 10^{-4}$ hartree and $|E_{\mathrm{OMM}}^{(3)}| \leq 2.8457 \times 10^{-6}$ hartree, which should be compared to the polarization energies and the conservative estimates shown in Table 1. As the table reveals, however, in general the upper bound provided by Eq. (31) is much too high compared to the absolute magnitude of the polarization energy of a given order.

For a couple of basis sets it was found that $R_{\mathrm{conv}}^{(100)} > 5$ bohr. These cases correspond with relatively large values of E_{OMM}, which, remember, is obtained from diagonalization of the total Hamiltonian, and not by summing the polarization series. While the second- and third-order polarization energies at $R = 5$ bohr are all reasonably small and not too strongly basis set dependent, one could expect that the higher-order polarization energies at $R = 5$ bohr will become larger and larger in these cases, since convergence of the polarization series itself is no longer guaranteed. This is indeed the case. To give an example, for the 9s7p5d3f basis set one finds $E_{\mathrm{OMM}}^{(10)} = -1.0375 \times 10^{13}$ hartree, $E_{\mathrm{OMM}}^{(20)} = -1.4899 \times 10^{36}$ hartree, $E_{\mathrm{OMM}}^{(30)} = -2.1394 \times 10^{59}$ hartree, etc., providing strong numerical evidence for a divergence of the polarization series in that case. Remembering that $E_{\mathrm{OMM}}^{(n)}$ is the limit of the $1/R$ expansion of $E_{\mathrm{pol}}^{(n)}$ for the given basis set, these results clearly demonstrate that the $1/R$-expanded polarization series can diverge though each of its members has a convergent multipole expansion. Nevertheless, when a finite-dimensional basis set is used one can always define an infinite-order (in n) $1/R$-expanded interaction energy E_{OMM}, from diagonalization of a Hamiltonian operator which includes the limit (in L) of the $1/R$-expanded interaction matrix, but a $1/R$-expanded polarization series, in general, will only converge to it when Eq. (30) is fulfilled.

While the infinite-order (in n), infinite-power (in L), interaction energy E_{OMM} will always be a finite number under the conditions of theorem 6, one observes from the results collected in Table 1 that this number becomes larger when the basis set size is systematically increased. This demonstrates that the multipole expansion of intermolecular interaction energies in a complete, infinite-

dimensional basis set can at most be asymptotically convergent, in agreement with theorem 1.

On the other hand, on looking at the variation of the second-order polarization energies, $E^{(2)}_{\mathrm{OMM}}$, with the basis set one could get the impression that they converge when the basis set size is increased, in contradiction to theorem 2. Yet, this is only a consequence of the fact that Table 1 only contains results obtained with up to f functions at most. With up to f functions only, the second-order induction energy will contain terms in $1/R$ with a power of up to $1/R^{14}$. The exact induction energy for $R = 5$ bohr up to this power of $1/R$ was calculated to be -9.2694×10^{-3} hartree by Dalgarno and Lewis [9]. This is more than twice the value obtained with the largest basis set used here. Part of the deviation of the basis set result from the exact one is due to contributions of the continuum wavefunctions to the latter. In Ref. [9] the continuum contributions were found to be responsible for an error of a factor of 2 at most. Another part of the deviation comes from the neglect of certain terms of order $1/R^{14}$ (and less) in the OMM value, which, for example, contains no 2^5-pole–2^7-pole polarizabilities owing to the limitation of f functions, while the remaining part is due to inexactness of the polarizabilities as calculated with the basis set. The divergence of the exact multipole-expanded induction energy will show up only for much larger powers of $1/R$: the contribution of order $1/R^{22}$ is -4.9047×10^{-2} hartree, that of order $1/R^{24}$ is 0.24442 hartree, and that of order $1/R^{26}$ is 1.44771 hartree [9]. In a basis set expansion one needs to go up to very high angular momentum functions (i functions and higher) to see the beginning of $E^{(2)}_{\mathrm{OMM}}$ divergence upon basis set extension.

Let us finally remark that for the atom–proton interaction the considerations presented here are not only valid for GTF or STF basis sets, but also for square-integrable functions with other radial dependencies. It is only necessary that those basis sets are finite-dimensional and that they possess well-defined angular momentum properties.

5 Summary and conclusions

It was shown that the validity of theorem 6 is a direct consequence of the convergence of $1/R$ expanded interaction energies between elementary charge distributions. In the proof it was implied that the zeroth-order polarization function is given by the product of the full CI ground state wavefunctions of both molecules and that the entire space spanned by all products of the ground-state and excited-state full CI wavefunctions is available for expansion of the higher-order polarization corrections. This is equivalent to assumimg that full CI charge densities and response properties are available. Yet, at least for the first- and second-order contributions this is not essential: any quantum chemical method which employs finte-dimensional, one-particle basis sets leads to an expansion of the electronic charge density, $\rho_{\mathrm{el}}(\mathbf{r})$, in ECDs $\chi^*_{\mathrm{a}}(\mathbf{r})\chi_{\mathrm{b}}(\mathbf{r})$, and the (frequency-dependent) first-order polarization propagator, $\Pi(\mathbf{r}, \mathbf{r}'; \omega)$, entering the calculation of the second-order induction and dispersion energies [3] can always be expanded in a finite number of products of ECDs such as $\chi^*_{\mathrm{a}}(\mathbf{r})\chi_{\mathrm{b}}(\mathbf{r})\chi^*_{\mathrm{c}}(\mathbf{r}')\chi_{\mathrm{d}}(\mathbf{r}')$. Therefore, one can also use multipole moments and polarizabilities from more approximate schemes, such as Hartree–Fock, density functional, Møller–Plesset or coupled-cluster methods to calculate $1/R$-expanded first- and second-order interaction energies and one can still be sure that they will converge with increasing L – as long as the conditions of theorem 6 are fulfilled and the basis set is left unaltered. Similar arguments can be put forward for higher-order induction energies and the third-order induction–dispersion contributions, i.e., those contributions which can be calculated from molecular higher-order (frequency-dependent) polarizabilities [3].

Furthermore, with GTF or STF basis sets there is not only a limit of the $1/R$ expansion for each nth-order contribution of the polarization series but one can also define a $1/R$-expanded interaction energy of infinite order in n. This is achieved by diagonalizing the matrix of a Hamiltonian operator which includes the $1/R$-expanded interaction terms. The infinite-order interaction energy will converge with increasing powers, L, of $1/R$ under the same conditions as the individual polarization contributions will converge. This does not imply, however, that the $1/R$-expanded polarization series will converge with increasing n, and it is important to clearly distinguish between convergence in L and convergence in n. Convergence in n to the infinite-order interaction energy is only guaranteed when the difference between the highest and lowest eigenvalues of the $1/R$-expanded interaction matrix is smaller than the excitation energy of the first mutipole-allowed transition, otherwise the series may diverge. Since the difference between the eigenvalues of the interaction matrix will become smaller and smaller with increasing intermolecular distance, this convergence criterion may be converted into a convergence radius, which will depend on the highest power of the $1/R$-expanded interaction matrix employed.

The hydrogen atom perturbed by a proton served for illustration. Here, as for all atom–atom interactions, it is particularly easy to reach the limit $L = \infty$ since the multipole expansion will terminate at some L which depends on the highest angular momentum of the basis function set employed. The $1/R$ expansion of the nth-order polarization energy contribution and of the infinite-order interaction energy therefore trivially converges with increasing L for each distance between the nuclei larger than zero. The $1/R$-expanded polarization series itself, however, converges with n only outside a certain radius, which strongly depends on the basis set and tends to become larger and larger upon augmentation with diffuse and high angular momentum basis functions.

This brings us to the last point: convergence with the size of the basis set. The limit of the $1/R$-expanded nth-order polarization energies depends on the basis set employed. It represents the exact multipolar contribution to the polarization energy for that particular basis set, but that does not imply that there exists a limit for the multipolar expansion of the exact nth-order polarization energy or of the exact total interaction energy. In

fact, according to theorems 2–4 these limits, in general, will not exist. This was clearly reflected in the increasing infinite-order polarization energies for the $H + H^+$ example when the basis set was augmented. Observation of the same effect for the second- and third-order polarization energies, however, would have required inclusion of much larger basis sets than those considered here.

For modeling intermolecular interaction potentials it is nearly always very useful to distinguish between long-range multipole interactions and exponentially decreasing short-range interactions. Part of these short-range interactions are the so-called penetration energies [13], which represent the difference between the $1/R$-expanded polarization energies and their nonexpanded counterparts. Clearly, divergence of the $1/R$ expansion makes this a somewhat problematic concept, and it is gratifying to see that multipolar and penetration contributions can at least be cleanly defined when finite-dimensional GTF or STF basis sets are used and that they can be deduced, in practice, from the interactions between OMM distributions corresponding to ECDs.

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