CONVERGENCE BEHAVIOR OF SYMMETRY-ADAPTED PERTURBATION EXPANSIONS FOR EXCITED STATES. A MODEL STUDY OF INTERACTIONS INVOLVING A TRIPLET HELIUM ATOM

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Dedicated to Professor Rudolf Zahradník on the occasion of his 75th birthday.

The convergence behavior of symmetry-adapted perturbation theory (SAPT) expansions is investigated for an interacting system involving an excited, open-shell monomer. By performing large-order numerical calculations for the interaction of the lowest, 1s2s, triplet state of helium with the ground state of the hydrogen atom we show that the conventional polarization and symmetrized Rayleigh–Schrödinger expansions diverge in this case. This divergence is attributed to the continuum of intruder states appearing when the hydrogen electron is falling on the helium 1s orbital and the 2s electron is ejected from the interacting system. One of the dimer states resulting from the interaction becomes then a resonance, which presents a hard case to treat by a perturbation theory. We show that the SAPT expansions employing the strong symmetry-forcing procedure, such as the Eisenschitz–London–Hirschfelder–van der Avoird or the Amos–Musher theories, can cope with this situation and lead to convergent series when the permutational symmetry of the bound, quartet state is forced. However, these theories suffer from a wrong asymptotic behavior of the second- and higher-order energies when the interatomic distance R grows to infinity, which makes them unsuitable for practical applications. We show that by a suitable regularization of the Coulomb potential and by treating differently the regular, long-range and the singular, short-range parts of the interatomic electron-nucleus attraction terms in the Hamiltonian one obtains a perturbation expansion which has the correct asymptotic behavior in each order and which converges fast for a wide range of interatomic distances.

Keywords: Weak interactions; Hamiltonian; Schrödinger equation; FCI calculations; Amos–Musher theory; Quantum chemistry.

Quantitative information about weak interatomic and intermolecular interactions is indispensable for a proper understanding and interpretation of a vast area of phenomena in molecular physics, physical chemistry, and biochemistry[1]. The progress in these disciplines depends, thus, to a large ex-

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tent on our ability to reliably predict the energies of intermolecular interactions. Two general theoretical approaches are available to make such predictions: the supermolecular method[2–4], in which the interaction energy is obtained as the difference between the energy of the dimer (supermolecule) and the sum of monomer energies, and the perturbation approach[5–7] providing the interaction energy directly as a sum of perturbation corrections of increasing order with respect to the operator V responsible for the intermolecular interaction phenomenon. Both approaches have their merits and problems[8,9]. The attractive features of the supermolecular method are its conceptual simplicity, universality, and possibility of a systematic improvement of the results by employing increasingly advanced levels of the electronic structure theory, see, *e.g.*, refs[10,11]. The supermolecular calculations have to rely, however, on a fortunate cancellation of large absolute errors (which does not always take place[12]) and encounter problems when the employed electronic structure method is not size-consistent[13] and/or when the elimination of the basis set superposition error[3] (BSSE) is not straightforward[4]. The main advantages of the perturbation theory approach are its high accuracy at large intermolecular separations, clear physical interpretation of the individual energy corrections, and well understood relation between these corrections and the monomer properties[14], which often enables an easy and qualitatively correct determination of the optimal structure of intermolecular complexes, see, *e.g.*, refs[15–17]. The drawbacks of the perturbation theory are its complex formal structure[18] and the potential loss of accuracy at smaller intermolecular distances, when the neglected higher-order corrections must become important[19–23]. It should be noted that there exist intimate relations between the supermolecular and perturbation methods[2,24] and one may argue that only a simultaneous application of both approaches can give a complete picture of the intermolecular interaction phenomenon.

It has been known for a long time[25,26] that the conventional Rayleigh–Schrödinger (RS) perturbation theory (referred to as the polarization expansion in the present context) employing the sum of the monomer Hamiltonians H_A and H_B as an unperturbed operator H_0 and the intermolecular interaction operator V as a perturbation is inadequate since it is not able to predict the very existence of the exchange contribution to the interaction energy. Many alternative perturbation schemes have been proposed in the literature to cope with this difficulty. The formal structure of these schemes, referred to as the symmetry-adapted perturbation theory (SAPT) expansions, has been discussed in some detail in refs[5,8,9,27]. One of the simplest SAPT formulations, the so-called symmetrized Rayleigh–Schrödinger

(SRS) expansion[28], has turned out to give good accuracy already through second order and has been implemented in a general utility computer program[29] applicable to interactions of closed-shell monomers.

Despite its numerous successful applications[7], the SRS version of SAPT cannot be viewed as entirely satisfactory. According to the arguments given by Adams[22,23] and confirmed recently in large-order numerical calculations[30], the SRS expansion must diverge when one of the monomers has three or more electrons. It might seem that this divergence should prevent a systematic improvement of the second-order SRS treatment by including higher order perturbation corrections. However, the arguments of Adams do not apply to the SAPT expansion suggested by Kolos and by one of the present authors[25] and developed fully in ref.[28] This expansion, referred to as the JK expansion. coincides with the SRS expansion through the second order and, as recently shown in large-order numerical calculations[31], converges when one of the monomers has more than two electrons, providing in this way a systematic procedure to improve on the second-order SRS results.

Despite the obvious spectroscopic importance of interatomic or intermolecular interactions involving electronically excited monomers, very little is known about the applicability of SAPT to dimers in electronically excited states. This is perhaps not surprising since the exchange effects in excited states are much stronger and can be expected to be more difficult to describe than in the ground state. In 1979 van Hemert and van der Avoird[32] applied a simple version of SAPT to the excited water dimer. They considered only the first-order effects (including exchange) and did not formulate a complete SAPT expansion. Soon after that Chalasinski and Szalewicz[33] developed two SAPT expansions which can be viewed as degenerate state generalizations of the Eisenschitz–London–Hirschfelder–van der Avoird[34–36] (ELHAV) and Murrell–Shaw–Musher–Amos[37,38] (MSMA) theories. Unfortunately, the convergence tests performed for several excited states of the H_2^+ ion have shown that both expansions diverge for all interatomic distances[33]. More recently, Korona *et al.*[39] used the wave operator technique to formulate three SAPT expansions applicable to interactions of degenerate and quasidegenerate states. Numerical calculations for the interaction of a ground-state helium atom with an excited hydrogen atom showed good convergence for the resulting $^2\Pi$ and $^2\Delta$ states. However, for the excited $A^2\Sigma^+$ state the convergence was only moderately good and for the $C^2\Sigma^+$ state – poor. The unsatisfactory convergence for the latter state was attributed to the effect of higher Rydberg states acting as intruders[39].

In the present work we intend to investigate the performance of SAPT for a very different kind of excited state, namely for the dimer involving an excited helium atom in the 1s2s ^{3}S state and a ground-state hydrogen atom. On the one hand, this system is simpler than the one considered in ref.[39] since it does not exhibit the orbital degeneracy. On the other hand, it is considerably more difficult since the excitation energy is much higher, in fact, higher than the ionization energy of the hydrogen atom. As a consequence, one of the two quasidegenerate dimer states resulting from the interaction – the doublet state – becomes a narrow resonance decaying *via* the Penning ionization mechanism[40]. The other state – the quartet – remains electronically bound (within the nonrelativistic theory) and exhibits a shallow van der Waals well. Thus, the potential energy curve for the fully antisymmetric quartet state is submerged in the continuum of doublet states of different permutational symmetry. This continuum can be viewed as an infinite family of intruder states and it is clear that in such circumstances any perturbation theory formalism must have great difficulty to converge to the exact bound-state solution of the Schrödinger equation. It should be mentioned that this is not an unusual situation in the theory of intermolecular forces. As emphasized by Adams[19,20], for all dimers containing monomers with more than two electrons the physical ground state is submerged in the continuum of Pauli forbidden states. The helium atom in the 1s2s ^{3}S state interacting with the ground-state hydrogen atom represents actually the simplest system for which the bound state resulting from the interaction is submerged in the continuum (in this case physical) of states of different permutational symmetry.

In this communication we present the results of large-order SAPT calculations for the lowest quartet state of HeH performed using the conventional SRS, ELHAV, and JK formulations, as well as the method of Amos and Musher[41] (AM) recommended by Adams[23] as an appropriate procedure for states submerged in the Pauli forbidden continuum. We shall also test three SAPT procedures involving a short-range attenuation of the attractive interatomic Coulomb terms in the Hamiltonian. Such an attenuation, achieved by a simple regularization procedure, was recently proposed by Patkowski *et al.*[42] and by Adams[43] to eliminate the pathologically slow convergence or divergence of SAPT expansions. All perturbation calculations will be done using a finite, carefully optimized basis set and the results will be compared with the full configuration interaction (FCI) interaction energies computed using the same basis set and counterpoise corrected for the BSSE [3].

CONVENTIONAL SAPT EXPANSIONS

The nonrelativistic clamped-nuclei Hamiltonian of two interacting atoms A and B with atomic numbers Z_A and Z_B, respectively, can be naturally partitioned as

$$H = H_0 + V, \tag{1}$$

where the unperturbed (zeroth-order) Hamiltonian H_0, describing the non-interacting atoms, is given by the sum

$$H_0 = H_\mathrm{A} + H_\mathrm{B} \tag{2}$$

of atomic Hamiltonians H_X, X = A, B,

$$H_X = \sum_{i \in X} \left(-\frac{1}{2} \Delta_i - \frac{Z_X}{r_{Xi}} \right) + \sum_{i<j \in X} \frac{1}{r_{ij}}, \tag{3}$$

r_{pq} denoting the distance between particles p and q, and the interaction operator V takes the form

$$V = \frac{Z_\mathrm{A} Z_\mathrm{B}}{r_\mathrm{AB}} - \sum_{i \in \mathrm{A}} \frac{Z_\mathrm{B}}{r_{\mathrm{B}i}} - \sum_{j \in \mathrm{B}} \frac{Z_\mathrm{A}}{r_{\mathrm{A}j}} + \sum_{i \in \mathrm{A}} \sum_{j \in \mathrm{B}} \frac{1}{r_{ij}}. \tag{4}$$

In Eqs (*3*) and (*4*), and throughout the entire text, atomic units are used. It is important to note that when defining the zeroth-order operator H_0 we had to arbitrarily assign certain electrons, *e.g.*, those labeled by 1, 2, ..., N_A, to atom A and the remaining ones, *e.g.*, those labeled by $N_\mathrm{A} + 1$, $N_\mathrm{A} + 2$, ..., $N_\mathrm{A} + N_\mathrm{B}$, to atom B. This fact has profound consequences, namely, H_0 treats electrons as distinguishable particles and its eigenfunctions do not satisfy the Pauli exclusion principle. In fact, the conventional Hilbert space $\mathcal{H}_\mathrm{AB}$ of all N-electron ($N = N_\mathrm{A} + N_\mathrm{B}$) wave functions of the dimer is not invariant under the action of H_0, so this operator must be considered as acting in a larger Hilbert space. Since the eigenfunctions of H_0 are of the form of the products $\phi_\mathrm{A}\phi_\mathrm{B}$, where ϕ_A and ϕ_B are eigenfunctions of H_A and H_B, respectively, it is clear that we must treat H_0 as acting in the space $\mathcal{H}_\mathrm{A} \otimes \mathcal{H}_\mathrm{B}$, the tensor product of Hilbert spaces $\mathcal{H}_\mathrm{A}$ and $\mathcal{H}_\mathrm{B}$ for subsystems A and B, respectively. When complete, or the so-called dimer-centered[3] basis sets are used in $\mathcal{H}_\mathrm{A}$ and $\mathcal{H}_\mathrm{B}$, then $\mathcal{H}_\mathrm{AB}$ is a subspace of $\mathcal{H}_\mathrm{A} \otimes \mathcal{H}_\mathrm{B}$.

The polarization expansion for the interaction energy and for the dimer wave function is obtained if the Hamiltonian H is parametrized as $H = H_0 + \lambda V$ and the resulting Schrödinger equation

$$(H_0 + \lambda V)\psi(\lambda) = E(\lambda)\psi(\lambda) \tag{5}$$

is solved by expanding $\psi(\lambda)$ and $E(\lambda)$ as power series in λ, *i.e.*, by assuming that $\psi(\lambda)$ and $E(\lambda)$ can be developed as convergent series

$$\psi(\lambda) = \psi^{(0)} + \lambda\psi^{(1)} + \lambda^2\psi^{(2)} + \ldots, \tag{6}$$

$$E(\lambda) = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \ldots. \tag{7}$$

Note that the operator $H(\lambda) = H_0 + \lambda V$ has the same symmetry properties as H_0, so for $\lambda \neq 1$ the eigenfunction $\psi(\lambda)$ does not belong to $\mathcal{H}_{AB}$ but to the larger space $\mathcal{H}_A \otimes \mathcal{H}_B$. When $\lambda = 0$, one obtains the zeroth-order equation $H_0\psi^{(0)} = E^{(0)}\psi^{(0)}$, which has a solution

$$\psi^{(0)} = \phi_A\phi_B, \qquad E^{(0)} = E_A + E_B, \tag{8}$$

where ϕ_A and ϕ_B are wave functions of the atomic states into which the dimer dissociates and E_A and E_B are the energies of these states, *i.e.*, $H_X\,\phi_X = E_X\,\phi_X$, X = A, B. We assume that the eigenvalue $E^{(0)}$ is nondegenerate or can be made nondegenerate by restricting our considerations to functions $\psi(\lambda)$ of specific symmetry with respect to the symmetry group of $H(\lambda)$. Under this assumption, the perturbation energies $E^{(n)}$ and wave functions $\psi^{(n)}$, n = 1, 2, ..., can be computed from the well-known recurrence relations of the Rayleigh–Schrödinger perturbation theory

$$E^{(n)} = \langle\phi_0|V\psi^{(n-1)}\rangle, \tag{9}$$

$$\psi^{(n)} = -R_0V\psi^{(n-1)} + \sum_{k=1}^{n} E^{(k)}R_0\psi^{(n-k)}, \tag{10}$$

where $\psi^{(0)} \equiv \phi_0$ and R_0 is the reduced resolvent of H_0 defined, *e.g.*, by

$$R_0 = (1 - P_0)(H_0 - E^{(0)} + P_0)^{-1}, \qquad P_0 = |\phi_0\rangle\langle\phi_0|. \tag{11}$$

In practice the evaluation of the resolvent operator R_0 is usually too complicated and is avoided by determining $R_0 f \equiv g$ from the linear equation $(H_0 - E^{(0)} + P_0)g = (1 - P_0)f$. If the series (*6*) converges at $\lambda = 1$, the interaction energy $\mathcal{E}$, defined as $\mathcal{E} = E(1) - E_A - E_B$, can be expanded as the sum $E^{(1)} + E^{(2)} + E^{(3)} + \dots$.

When λ varies from 0 to 1, the functions $E(\lambda)$ and $\psi(\lambda) \in \mathcal{H}_A \otimes \mathcal{H}_B$ provide a correlation between the eigenvalue $E(0) = E_A + E_B$ and eigenfunction $\psi(0) = \phi_A\phi_B$ of H_0 on the one hand and certain eigenvalue $E(1)$ and eigenfunction $\psi(1) \in \mathcal{H}_A \otimes \mathcal{H}_B$ of H on the other. This correlation gives an important qualitative information about the function $E(\lambda)$ and about a possible convergence radius of the series (*6*) and (*7*). To illustrate this point, we shall consider specifically the interaction of a triplet helium atom with a hydrogen atom. Assuming that all spins in the system are aligned, we can factorize the spin part of the wave function and work only with spatial wave functions. The Hilbert space $\mathcal{H}_A$ consists then of all antisymmetric functions $\phi(\boldsymbol{r}_1,\boldsymbol{r}_2)$ of the spatial electronic coordinates $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$, while $\mathcal{H}_A \otimes \mathcal{H}_B$ is a space of all three-electron functions $\phi(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{r}_3)$ which are antisymmetric when the position vectors $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ are interchanged. The spectra of H_0 (left bar diagram) and of H (right bar diagram) in $\mathcal{H}_A \otimes \mathcal{H}_B$, computed for a large interatomic distance $R = 12.5$ bohr, are shown in Fig. 1. The correlation between the two lowest levels of these spectra (*via* $E(\lambda)$) and between the corresponding ionization thresholds is also indicated. It is seen that at λ equal to about 0.7 the ground-state energy of $H_0 + \lambda V$ undergoes an abrupt change and at $\lambda = 1$ the spectrum is qualitatively different from the spectrum of H_0. This change corresponds to the fall of the electron number 3 from the hydrogen to the helium 1s orbit and a simultaneous transfer of the 2s electron from the helium to the hydrogen atom. The ionization threshold of $H_0 + \lambda V$ also collapses but at a slightly larger value of λ. As a result, the lowest quartet level of H, visible on the r.h.s. of Fig. 1 at about the same position as the unperturbed energy $E^{(0)}$, is submerged in the continuum of states of the permutational symmetry corresponding to the spin doublet. Figure 1 also shows that the difference $E(1) - E^{(0)}$ is very large and does not vanish for large R, so this difference cannot be taken as a definition of the interaction energy. It is clear that V, having such a dramatic effect on the spectrum of H_0, cannot be viewed as a small perturbation and the corresponding RS perturbation series (*i.e.*, the polarization expansion) cannot be expected to converge at $\lambda = 1$.

The abrupt downward bend of the ground-state energy, visible in Fig. 1, is due to the sharp avoided crossing with the first excited state. For the interatomic separation of $R = 12.5$ bohr (corresponding to the minimum of the van der Waals well in the lowest quartet state) this avoided crossing occurs at $\lambda = 0.719$. Its position increases somewhat with R and approaches 0.740 as R grows to infinity. A sharp avoided crossing, such as the one visible in Fig. 1, is a manifestation of the presence of a conjugate pair of branch-point-type singularities located very close to the real axis. Therefore, the convergence radius of the polarization expansion, bounded from above by the modulus of these singularities, cannot be greater than 0.740 at large R.

The SRS Theory

The simplest SAPT approach which for closed-shell monomers gives a good accuracy already in the second order[7] is the SRS theory. The SRS perturbation series is derived by employing the following interaction energy expression[28]

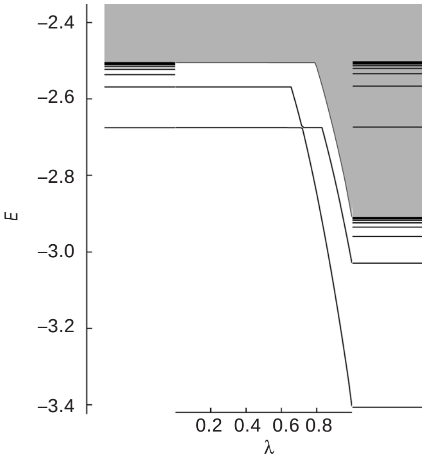

FIG. 1
Spectra of H_0 (left bar diagram) and of H (right bar diagram) in $\mathcal{H}_A \otimes \mathcal{H}_B$. The correlation between these spectra is shown by plotting the lowest two levels and the ionization threshold of $H_0 + \lambda V$ as a function of λ. The unit of energy is hartree. The interatomic distance is $R = 12.5$ bohr

$$E_{\mathrm{SRS}}(\lambda) = \frac{\langle \phi_0 | \lambda V \mathcal{A} \psi(\lambda) \rangle}{\langle \phi_0 | \mathcal{A} \psi(\lambda) \rangle}, \tag{12}$$

where $\mathcal{A}$ is the antisymmetrizer (or other appropriate symmetry projector) and $\psi(\lambda)$ is a solution of Eq. (*5*), and by expanding $E_{\mathrm{SRS}}(\lambda)$ in powers of λ: $E_{\mathrm{SRS}}(\lambda) = \lambda E^{(1)}_{\mathrm{SRS}} + \lambda^2 E^{(2)}_{\mathrm{SRS}} + \dots$. The recurrence equations for the SRS perturbation energies $E^{(n)}_{\mathrm{SRS}}$ are[28]

$$E^{(n)}_{\mathrm{SRS}} = N_0[\langle \phi_0 | V \mathcal{A} \psi^{(n-1)} \rangle - \sum_{k=1}^{n-1} E^{(k)}_{\mathrm{SRS}} \langle \phi_0 | \mathcal{A} \psi^{(n-k)} \rangle], \tag{13}$$

where $N_0 = \langle \phi_0 | \mathcal{A} \phi_0 \rangle^{-1}$ and $\psi^{(n)}$ are the perturbation corrections to the wave function in the RS perturbation theory, given by Eq. (*10*). SRS is an example of the so-called weak symmetry-forcing procedure[9,25], because the antisymmetrization operator appears only in the energy expression, while the equations for the perturbed wave function do not contain any symmetry projection.

The expression (*12*) had been proposed[28] before it was discovered that the series (*6*) is usually divergent[26] at $\lambda = 1$. Despite its divergence, the SRS expansion has turned out to provide, somewhat surprisingly, very good results in low-order calculations[7,30,44]. Very good results at large distances are understandable since the SRS theory is consistent[27] with the exact asymptotic expansion of the interaction energy[45] in powers of $1/R$ (this means that each van der Waals constant can be obtained in a finite-order SRS treatment). Good representation of the exchange part of the interaction energy does not have such a theoretical foundation. However, based on the results of numerical calculations[30] for the interaction of the ground-state lithium and hydrogen atoms, it appears that a very good approximation to the exchange energy can be obtained at large R using a finite-order SRS treatment.

The ELHAV Theory

The ELHAV theory is the oldest[34] SAPT formulation. Numerous different derivations of this theory have been given in the literature[28,34–36,46]. We believe that the formulation of ref.[28], based on the idea of forcing the symmetry in an iterative solution of the Bloch form[47] of the Schrödinger equation, reflects best the essential idea of this method. The nondegenerate Bloch equation, equivalent to Eq. (*5*) when $\lambda = 1$, is

$$\psi = \phi_0 + R_0(\mathcal{E} - V)\psi \tag{14}$$

$$\mathcal{E} = \langle \phi_0 | V \psi \rangle , \tag{15}$$

where $\psi = \psi(1)$ and where, as always in the Bloch theory, the intermediate normalization $\langle \phi_0 | \psi \rangle = 1$ is assumed. It is well known that by iterating Eqs (*14*) and (*15*) using ϕ_0 as an initial approximation to ψ one obtains the usual RS perturbation expansion[25]. We know, however, that because of its incorrect permutational symmetry the function ϕ_0 is always a poor[25] approximation to ψ. A much better starting point for the iterations would be the function

$$\psi_0 = N_0 \mathcal{A} \phi_0 , \tag{16}$$

which approximates ψ very well at large R, in the sense that[27] $||\psi_0 - \psi|| = O(R^{-3})$ (for neutral monomers). Iterating Eqs (*14*) and (*15*) using ψ_0 as a starting point leads to the MSMA theory[25], which still diverges in most cases[31,48]. The reason of this divergence is the fact that the r.h.s. of Eq. (*14*) does not preserve the symmetry of ψ. This problem can be circumvented if the correct symmetry is forced in each step of the iterations, *i.e.*, if Eqs (*14*) and (*15*) are replaced by the projected Bloch equation

$$\psi = \phi_0 + R_0(\mathcal{E} - V)\mathcal{A}\psi , \tag{17}$$

$$E = \frac{\langle \phi_0 | V \mathcal{A} \psi \rangle}{\langle \phi_0 | \mathcal{A} \psi \rangle} . \tag{18}$$

The denominator in Eq. (*18*) was introduced to take care of the fact that the symmetry projection does not conserve the intermediate normalization, *cf.*, Eq. (*12*). The ELHAV expansion is obtained by iterating Eqs (*17*) and (*18*) using ψ_0 of Eq. (*16*) to start the iteration process[28,31]. The recurrence equations for the resulting perturbation corrections $E^{(n)}_{\mathrm{ELHAV}}$ are[28]

$$E^{(n)}_{\mathrm{ELHAV}} = \langle \phi_0 | V \mathcal{A} \psi^{(n-1)}_{\mathrm{ELHAV}} \rangle - \sum_{k=1}^{n-1} E^{(k)}_{\mathrm{ELHAV}} \langle \phi_0 | \mathcal{A} \psi^{(n-k)}_{\mathrm{ELHAV}} \rangle , \tag{19}$$

where $\psi^{(0)}_{\mathrm{ELHAV}} = N_0 \mathcal{A} \phi_0$, $\psi^{(1)}_{\mathrm{ELHAV}} = N_0 R_0 \mathcal{A}(E^{(1)}_{\mathrm{ELHAV}} - V)\phi_0$, and

$$\psi^{(n)}_{\mathrm{ELHAV}} = -R_0 V \mathcal{A} \psi^{(n-1)}_{\mathrm{ELHAV}} + \sum_{k=1}^{n} E^{(k)}_{\mathrm{ELHAV}} R_0 \mathcal{A} \psi^{(n-k)}_{\mathrm{ELHAV}} \tag{20}$$

for $n \geq 2$. In a few model calculations performed thus far[28,31,42] the ELHAV method was shown to converge fast in high orders but was giving very poor results in a low-order treatment because of the well-known incorrect asymptotic behavior of the energy corrections at large interatomic separations[25,49,50].

The JK Theory

When the symmetry-forcing procedure characteristic of the ELHAV theory is relaxed by removing the antisymmetrizer $\mathcal{A}$ from the energy expression of Eq. (*18*) (as suggested in ref.[25]), and leaving it only in the wave function equation, Eq. (*17*), and when the resulting equations are solved by iteration using ψ_0 as a starting point, one obtains the JK expansion[28,31]. The resulting expression for the energy corrections $E^{(n)}_{\mathrm{JK}}$ is

$$E^{(n)}_{\mathrm{JK}} = \langle \phi_0 | V \psi^{(n-1)}_{\mathrm{JK}} \rangle, \tag{21}$$

where $\psi^{(0)}_{\mathrm{JK}} = N_0 \mathcal{A} \phi_0$, $\psi^{(1)}_{\mathrm{JK}} = \psi^{(1)}_{\mathrm{ELHAV}}$ and

$$\psi^{(n)}_{\mathrm{JK}} = -R_0 V \mathcal{A} \psi^{(n-1)}_{\mathrm{JK}} + \sum_{k=1}^{n} E^{(k)}_{\mathrm{JK}} R_0 \mathcal{A} \psi^{(n-k)}_{\mathrm{JK}} \tag{22}$$

for $n \geq 2$. It is easy to see that $E^{(1)}_{\mathrm{JK}} = E^{(1)}_{\mathrm{SRS}}$ and $E^{(2)}_{\mathrm{JK}} = E^{(2)}_{\mathrm{SRS}}$, so the JK method through the second order correctly predicts the leading terms of the large-R asymptotic expansion of the interaction energy (through $C_{10}R^{-10}$ for atom–atom interactions). It also appears[31] that its convergence radius (and, consequently, the high-order convergence rate) is practically the same as in the ELHAV method. Therefore, the JK method can be expected to give much more accurate results than both the SRS or ELHAV approaches.

The AM Theory

The AM theory is based on the observation[41] that, after antisymmetrization, a nonsymmetric eigenfunction ϕ of the Hamiltonian $H_{\mathrm{AM}} = H_0 + \mathcal{A}V$ becomes an eigenfunction of $H_0 + V$, *i.e.*, if $(H_0 + \mathcal{A}V)\phi = E\phi$ then $(H_0 + V)\mathcal{A}\phi = E\mathcal{A}\phi$. This means that ϕ is a primitive wave function[26], *i.e.*, a function from which the exact wave function is obtained by a symmetry projection. The AM theory had remained forgotten until Adams[23,43] made an important observation that $\mathcal{A}V$ should be a much weaker perturbation than V itself, so the spectra of H_0 and $H_0 + \mathcal{A}V$ should not differ as dramatically as the spectra of H_0 and $H_0 + V$. In particular, he observed that the continuous spectrum of $H_0 + \mathcal{A}V$ (in $\mathcal{H}_A \otimes \mathcal{H}_B$) starts much higher than the continuous spectrum of $H_0 + V$, and does not cover the physical ground state of the dimer. The AM expansion has not been applied thus far in a large-order calculation, so the present study represents the first test of the convergence of this method.

If $(H_0 + \mathcal{A}V)\phi = E\phi$ and $\mathcal{A}\phi \neq 0$ then the eigenvalue E represents the energy of the physical state of the dimer and the interaction energy can be computed directly by applying the RS perturbation theory to the (non-Hermitian) Hamiltonian $H_0 + \mathcal{A}V$ and treating $\mathcal{A}V$ as a perturbation. The resulting wave function and energy corrections can be obtained from the equations

$$E_{\mathrm{AM}}^{(n)} = \langle \phi_0 | \mathcal{A}V \psi_{\mathrm{AM}}^{(n-1)} \rangle , \tag{23}$$

$$\psi_{\mathrm{AM}}^{(n)} = -R_0 \mathcal{A}V \psi_{\mathrm{AM}}^{(n-1)} + \sum_{k=1}^{n} E_{\mathrm{AM}}^{(k)} R_0 \psi_{\mathrm{AM}}^{(n-k)} , \tag{24}$$

where $\psi_{\mathrm{AM}}^{(0)} \equiv \phi_0$. We found that the perturbation expansion for the energy, defined by Eqs (*23*) and (*24*), is convergent but the convergence is very slow. We also found that a dramatically better convergence is obtained if the perturbation series for the wave function, defined by these equations, is antisymmetrized (in the spirit of the SRS method) and used as ψ in the energy expression of Eq. (*18*). The resulting improved AM perturbation energies, defined by expanding Eq. (*18*) in powers of V and denoted by $E_{\mathrm{SAM}}^{(n)}$ (for the symmetrized AM expansion), can be obtained recursively from an SRS-like equation of the form

$$E_{\mathrm{SAM}}^{(n)} = N_0 [\langle \phi_0 | V \mathcal{A} \psi_{\mathrm{AM}}^{(n-1)} \rangle - \sum_{k=1}^{n-1} E_{\mathrm{SAM}}^{(k)} \langle \phi_0 | \mathcal{A} \psi_{\mathrm{AM}}^{(n-k)} \rangle] , \tag{25}$$

where the functions $\psi_{\mathrm{AM}}^{(n)}$ are defined by Eq. (*24*).

REGULARIZED SAPT EXPANSIONS

None of the SAPT expansions discussed in the preceding section, except for the divergent RS and SRS theories, is consistent with the large-R asymptotic expansion of the interaction energy[45]. This is due to the fact that the perturbation $\mathcal{A}V$, weakened by the action of the antisymmetrizer $\mathcal{A}$, differs significantly from V at large R. This problem can be circumvented by weakening only the short-range part of V and leaving the long-range part intact. The idea of treating the long- and the short-range parts of V differently, proposed by Adams[43,51], can be implemented in practice by the regularization technique of ref.[42] According to this reference the attractive Coulombic terms in the one-electron part of V are split as $r^{-1} = v_p(r) + v_t(r)$, where

$$v_p(r) = r^{-1}(1 - \mathrm{e}^{-\eta r^2}) \tag{26}$$

and

$$v_t(r) = r^{-1} - v_p(r) = r^{-1}\mathrm{e}^{-\eta r^2} \tag{27}$$

are the regular and singular parts of $1/r$, respectively. Different values of the regularization parameter η can be used for the Coulomb potentials of monomers A and B. Of course other regularization functions can also be used. One can set, *e.g.*, $v_p(r) = r^{-1}\,\mathrm{erf}\,(\sqrt{\eta}\,r)$ (for a review of other choices see ref.[52]), but we found that these other functions offer no real advantage over the simple choice of Eq. (*26*). One different choice, free from arbitrary parameters, will, however, be considered in part Smeared Nuclear Charge Regularization.

The regularization of the Coulomb potential leads to the following partitioning of the interaction operator V:

$$V = V_p + V_t\,, \tag{28}$$

where

$$V_t = -\sum_{i\in \mathrm{A}} Z_\mathrm{B} v_t(r_{\mathrm{B}i}) - \sum_{j\in \mathrm{B}} Z_\mathrm{A} v_t(r_{\mathrm{A}j}) \tag{29}$$

and

$$V_p = V - V_t\,. \tag{30}$$

The operator V_p may be viewed as being responsible for the mutual polarization of the electron clouds at both atoms and for the intermonomer correlation of electrons, while V_t for the resonance tunneling of electrons between interacting atoms, as indicated by the subscripts p and t.

Regularized SRS Theory

The simplest way to utilize the regularization and the resulting partitioning of V is to initially neglect the short-range part V_t. When V_t is neglected and when η is sufficiently small, the electrons from atom B are not attracted by a strongly negative Coulomb potential at the vicinity of the nucleus A. Consequently, the electron transfer leading to the dramatic variation of the function $E(\lambda)$ and to the low-lying continuum of different permutational symmetry is suppressed. The operator V_p can then be viewed as a small perturbation and one can expect that the RS perturbation procedure corresponding to the Hamiltonian partitioning $H_0 + \lambda V_p$, *i.e.*, the regularized RS (R-RS) expansion, will be convergent. Of course, the converged perturbed wave function $\psi_p(\lambda)$ will not have the correct permutational symmetry and will differ substantially for $\lambda = 1$ from the exact function $\psi(1)$. One can expect[53], however, that $\psi_p(1)$ will be for large R a good approximation to an exact primitive wave function from which $\psi(1)$ can be obtained by an appropriate symmetry projection, in our case by the action of the antisymmetrization operator $\mathcal{A}$. This means that the function $\mathcal{A}\psi_p(1)$ will be a good approximation to $\psi(1)$ and that the energy expression

$$E_{\text{R-SRS}}(\lambda) = \frac{\langle \phi_0 | \lambda V \mathcal{A} \psi_p(\lambda)\rangle}{\langle \phi_0 | \mathcal{A} \psi_p(\lambda)\rangle} \tag{31}$$

will give for $\lambda = 1$ a very good approximation to the exact interaction energy $\mathcal{E}$ (note that the full interaction operator V, rather than its polarization part V_p, is used in this energy formula). The corresponding regularized SRS expansion (R-SRS) is defined[42] by expanding Eq. (*31*) in powers of λ. The resulting expression for the n-th order R-SRS energy is

$$E^{(n)}_{\text{R-SRS}} = N_0 [\langle \phi_0 | V \mathcal{A} \psi_p^{(n-1)}\rangle - \sum_{k=1}^{n-1} E^{(k)}_{\text{R-SRS}} \langle \phi_0 | \mathcal{A} \psi_p^{(n-k)}\rangle], \tag{32}$$

where $\psi_p^{(n)}$ are the perturbed wave functions of the R-RS theory, *i.e.*, $\psi_p(\lambda) = \phi_0 + \lambda\psi_p^{(1)} + \lambda^2\psi_p^{(2)} + \dots$. Since the R-SRS and SRS energies differ only by some short-range terms (due to V_t), the R-SRS expansion has the same correct asymptotic behavior at large R as the SRS theory.

For η values of the order of unity, the R-SRS expansion for the triplet state of H_2 was shown[42] to converge very fast (unlike the conventional SRS expansion employing the full, nonregularized Coulomb potential) and its infinite-order sum represented about 98% of the exact interaction energy at the van der Waals minimum distance of $R = 8$ bohr. However, for two-electron systems the continuum of intruder states does not appear and the good performance of the R-SRS theory, observed for H_2, may not occur for larger systems. In fact, recent calculations[54] show that for the interaction of the ground-state lithium and hydrogen atoms the infinite-order R-SRS theory is substantially less accurate than for H_2.

Regularized SAM Theory

The R-SRS expansion correctly recovers the whole long-range asymptotics of the interaction energy and the major part of the exchange energy, but misses, even in infinite order, some exponentially vanishing, presumably small part of the interaction energy resulting from the presence of the operator V_t in the exact Hamiltonian. A method to correct the R-SRS expansion by including V_t *via* the symmetry-forcing procedure of the ELHAV theory was proposed in ref.[42], and developed further in ref.[54] In the present work we consider another method of including V_t, based on the SAM theory. The idea of this method – proposed by Adams[43] and referred to by him as the corrected SRS theory (cSRS) – is to weaken V_t by multiplying it by $\mathcal{A}$ and, then, to include $\mathcal{A}V_t$ in the perturbed Hamiltonian. Specifically, Adams proposed to apply the conventional RS perturbation theory to the equation

$$(H_0 + \lambda V_{\text{R-AM}})\,\phi(\lambda) = E_{\text{R-AM}}(\lambda)\,\phi(\lambda)\,, \tag{33}$$

where

$$V_{\text{R-AM}} = V_p + \mathcal{A}(V_t - D) \tag{34}$$

and $D = \langle \phi_0 | V_t \mathcal{A} \phi_0 \rangle / \langle \phi_0 | \mathcal{A} \phi_0 \rangle$. For $\lambda = 1$ this equation defines an exact primitive function $\phi(1)$. Since the perturbation V_p is small and the Coulomb singularities in $\mathcal{A}V_t$ are weakened (by the group theoretical normalization factor of $\mathcal{A}$), one can expect that the resulting RS expansion $\phi(\lambda) = \phi_0 + \lambda\phi^{(1)} + \lambda^2\phi^{(2)} + \ldots$ and the corresponding expansion for the interaction energy, defined as $E_{\text{R-AM}}(\lambda) + D$, will be convergent for $\lambda = 1$. We found that these expansions indeed converge but the perturbation series for $E_{\text{R-AM}}(\lambda)$ converges very slow at $\lambda = 1$. Much faster convergence is obtained if the interaction energy is defined by the SRS-like energy expression

$$E_{\text{R-SAM}}(\lambda) = \frac{\langle \phi_0 | \lambda V \mathcal{A} \phi(\lambda) \rangle}{\langle \phi_0 | \mathcal{A} \phi(\lambda) \rangle} . \tag{35}$$

The expansion of Eq. (*35*) in powers of λ leads to a perturbation expansion for the interaction energy which can be viewed as a regularized SAM (R-SAM) expansion. The specific expression for the *n*-th order R-SAM energy is

$$E^{(n)}_{\text{R-SAM}} = N_0 [\langle \phi_0 | V \mathcal{A} \phi^{(n-1)} \rangle - \sum_{k=1}^{n-1} E^{(k)}_{\text{R-SAM}} \langle \phi_0 | \mathcal{A} \phi^{(n-k)} \rangle] , \tag{36}$$

where $\phi^{(0)} \equiv \phi_0$. Since V_t is a short-range operator, it is easy to see that the corrections $E^{(n)}_{\text{R-SRS}}$ and $E^{(n)}_{\text{R-SAM}}$ differ by exponentially vanishing terms. Consequently, each correction of the R-SAM expansion has the correct asymptotic behavior at large *R*. Adams applied the R-SAM expansion (with a different regularization function) through the first order in the wave function obtaining only a marginal[43] improvement over the conventional SRS treatment. In the present work we shall report a large-order test of the R-SAM method.

Adams's Zero-Induction Theory

To improve the accuracy of his cSRS method at short interatomic distances, Adams proposed to reformulate it to include the induction effects in the zeroth order[43]. The formal scheme of his method, which he refers to as the ZI theory, is the same as the scheme of the R-SAM method except that the definitions of all operators are changed to include the effect of the induction interaction. The unperturbed operator H_0 is replaced by $\tilde{H}_0 = \tilde{H}_\text{A} + \tilde{H}_\text{B}$, where $\tilde{H}_\text{A} = H_\text{A} + \Omega_\text{B}$, $\tilde{H}_\text{B} = H_\text{B} + \Omega_\text{A}$, and

$$\Omega_\text{B} = -\sum_{i \in \text{A}} Z_\text{B} v_p (r_{\text{B}i}) + \sum_{i \in \text{A}} \int \frac{1}{r_{ij}} \rho^{(0)}_\text{B} (r_j)\, \mathrm{d} r_j \tag{37}$$

is the operator of the electrostatic potential of atom B resulting from the regularized Coulomb attraction of the nucleus and the repulsive potential of the electrons computed using the electron density $\rho^{(0)}_\text{B}(\boldsymbol{r}_j)$ of the unperturbed atom. The definition of Ω_A is obtained by interchanging A and B in Eq. (*37*). The unperturbed function ϕ_0 is replaced by the function $\tilde{\phi}_0 = \tilde{\phi}_\text{A} \tilde{\phi}_\text{B}$, where $\tilde{\phi}_X$, X = A, B, is the ground-state eigenfunction of $\tilde{H}_X$, *i.e.*,

$\tilde{H}_X \tilde{\phi}_X = \tilde{E}_X \tilde{\phi}_X$. The zeroth-order energy $E^{(0)}$ is accordingly replaced by $\tilde{E}^{(0)} = \tilde{E}_A + \tilde{E}_B$. The operator V_p is replaced by $\tilde{V}_p = V_p - \Omega_A - \Omega_B$ and the operator V_t remains unchanged, $\tilde{V}_t = V_t$. The perturbation expansion for the function $\tilde{\phi}(\lambda)$, defined by appropriately modified Eqs (*33*) and (*34*), can be obtained from the conventional equations of the RS perturbation theory involving the reduced resolvent $\tilde{R}_0$ defined by Eq. (*11*) with tildas added over all symbols.

With these substitutions, Eqs (*33*)–(*36*) uniquely define the perturbation energies $E_{ZI}^{(n)}$ of the ZI theory. The interaction energy $\mathcal{E}$ is obtained from the expression

$$\mathcal{E} = \tilde{E}^{(0)} - E^{(0)} + E_{ZI}^{(1)} + E_{ZI}^{(2)} + \dots , \qquad (38)$$

i.e., by adding the trivially computed difference of zeroth-order energies to the sum of the ZI corrections. It is worthwhile to note that the ZI method makes sense only with appropriately regularized Coulomb potential. Without regularization, the singular part of Ω_X would generate unphysical electron transfer between atoms and the new zeroth-order function $\tilde{\phi}_0$ would lose its similarity to ϕ_0.

It should be mentioned that Adams's formulation of the ZI method differs slightly from ours. Apparently for practical reasons, Adams included in $\tilde{H}_0$ a small singular term of the form $(N_A!N_B!/N!)V_t$ and subsequently subtracted it from $\tilde{V}_p$. We believe that this additional complication is unnecessary and we did not introduce it. Adams applied the ZI method through the first order in the wave function and obtained a significant improvement compared to the R-SAM method. In the present work we shall report a large-order test of the ZI method.

Smeared Nuclear Charge Regularization

One of the simplest methods of regularizing the Coulomb potential involves replacing the point-charge model of the nucleus by a nuclear charge smeared with a certain charge density distribution. We shall refer to this method as to the smeared nuclear charge (SNC) regularization. In fact, the potential regularized by the error function $r^{-1}\,\mathrm{erf}\,(\sqrt{\eta}\,r)$ can be viewed as resulting from the SNC described by the Gaussian distribution with $\sigma = 1/\sqrt{2\eta}$. A specific realization of the SNC regularization is obtained if the positive nuclear charge is smeared with the density equal exactly to the electronic density $\rho_X^{(0)}(\boldsymbol{r})$. The regularized potential v_p acting on the electrons, *e.g.*, of atom A, takes then the form

$$v_p(\boldsymbol{r}_i) = \frac{1}{Z_\mathrm{B}} \int \frac{1}{r_{ij}} \rho_\mathrm{B}^{(0)}(\boldsymbol{r}_j)\,\mathrm{d}\boldsymbol{r}_j\,. \tag{39}$$

The advantage of the potential of Eq. (*39*) is that it is defined by the intrinsic property of an atom and does not contain any arbitrary parameters. We tested the regularization defined by Eq. (*39*) in high-order R-SAM calculations. The resulting perturbation procedure turns out to be equivalent to the P1 method of ref.[51] and will be referred to as the SNC-P1 method. It is interesting to note that for v_p given by Eq. (*39*) the operators Ω_X of Eq. (*37*), and consequently, all induction effects vanish identically. Thus, the SNC-P1 method is invariant under the transformation described in the previous part leading from the R-SAM to the ZI method.

NUMERICAL PROCEDURE AND COMPUTATIONAL DETAILS

All SAPT calculations were performed using a finite orbital basis and were compared with FCI calculations employing the same basis. The basis set in $\mathcal{H}_\mathrm{A}$ consisted of functions of the form

$$\chi_{pq}(\boldsymbol{r}_1,\boldsymbol{r}_2) = \frac{1}{\sqrt{2}}[\chi_p(\boldsymbol{r}_1)\chi_q(\boldsymbol{r}_2) - \chi_p(\boldsymbol{r}_2)\chi_q(\boldsymbol{r}_1)], \quad 1 \le p < q \le m\,, \tag{40}$$

where the orbitals $\chi_1, ..., \chi_m$, assumed to form an orthonormal set, are constructed from a primitive set of atomic orbitals localized on both atoms and, possibly, in the middle of the line joining the atoms. Thus, we employed the so-called dimer-centered basis set[3] (DCBS) with midbond functions. Since the functions χ_{pq} are used to represent triplet wave functions, they are taken to be antisymmetric. Although this is not necessary, we used as χ_p the functions diagonalizing the Fock operator for the lowest triplet state of helium. The Hilbert space $\mathcal{H}_\mathrm{B}$ is spanned by the same set of m orthonormal one-electron functions χ_p. However, to simplify the solution of perturbation equations, it is convenient to diagonalize H_B and employ as the basis in $\mathcal{H}_\mathrm{B}$ the functions ϕ_r, satisfying $\langle \phi_r | H_\mathrm{B} \phi_s \rangle = \varepsilon_s \delta_{rs}$.

The basis set in $\mathcal{H}_\mathrm{A} \otimes \mathcal{H}_\mathrm{B}$ is the tensor product of the bases in $\mathcal{H}_\mathrm{A}$ and $\mathcal{H}_\mathrm{B}$ and consists of $m^2(m-1)/2$ functions of the form

$$\psi_{pqr}(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{r}_3) = \chi_{pq}(\boldsymbol{r}_1,\boldsymbol{r}_2)\,\phi_r(\boldsymbol{r}_3)\,. \tag{41}$$

This basis is orthonormal despite the lack of orthogonality between the basis functions χ_p and ϕ_r, *i.e.*, despite the fact that $\langle \chi_p | \phi_r \rangle = S_{pr} \neq 0$. Because of the relation $\langle \phi_r | H_B \phi_s \rangle = \varepsilon_r \delta_{rs}$, the matrix of $H_A + H_B$ computed with the basis ψ_{pqr} consists of m diagonal blocks of dimension $m(m - 1)/2$, which greatly simplifies the solution of the perturbation equations.

In SAPT calculations, we need to calculate matrix elements of the antisymmetrizer $\mathcal{A}$. Since $P_{12}\,\chi_{pq} = -\chi_{pq}$, where P_{12} is the permutation operator defined for any $\chi(\boldsymbol{r}_1,\boldsymbol{r}_2)$ as $(P_{12}\chi)\,(\boldsymbol{r}_1, \boldsymbol{r}_2) = \chi(\boldsymbol{r}_2,\boldsymbol{r}_1)$, the operator $\mathcal{A}$, when acting on functions from $\mathcal{H}_A \otimes \mathcal{H}_B$, can be written in the form $(1 - P_{13} - P_{23})/3$. When $P_{13} + P_{23}$ acts on the basis function ψ_{pqr}, it produces a function which is not an element of the basis set of Eq. (*41*). However, $(P_{13} + P_{23})\psi_{pqr}$ can easily be expressed in terms of this basis by using the unitary transformation

$$\chi_p = \sum_{r=1}^{m} S_{pr}\phi_r\,, \qquad \phi_r = \sum_{p=1}^{m} S_{pr}\chi_p\,, \tag{42}$$

where we assumed that the overlap matrix S_{pr} is real. Thus, by construction, the space $\mathcal{H}_A \otimes \mathcal{H}_B$ is invariant under the action of $\mathcal{A}$. This invariance is necessary to guarantee that a finite basis set SAPT calculation converges to the counterpoise corrected[3] FCI interaction energy computed with the same basis set[44].

The computer code developed to perform calculations reported in this work is similar in its salient features to the code used in ref.[30] and we refer the reader to this reference for some details supplementing the information given further on in this section.

One-Electron Basis Set and Integral Evaluation

All FCI and perturbation calculations were performed with three dimer-centered basis sets developed specifically for these calculations. The smallest basis, referred to as B61, consisted of 7s5p3d basis on helium and 5s3p2d basis on hydrogen. By adding to B61 the 3s3p2d part (22 functions) of the 3s3p2d1f1g midbond set from ref.[55] we obtained the basis B61+22b. Finally, our largest basis, referred to as B106, consisted of 7s7p5d2f basis on helium and 5s4p3d1f basis on hydrogen. The 7s set for helium is a contraction of a 30s set obtained by a full nonlinear optimization of the Hartree–Fock energy for the lowest triplet state of helium. Analogously, the 5s set for hydrogen is a contraction of the 29s basis obtained from the formula recommended by Morgan and Haywood[56] for an accurate representation of the 1s hydrogen orbital. The exponents and the contraction coefficients of the *s* functions can be supplied upon request.

The exponents of the polarization functions, listed in Table I, were obtained in the following way. The three largest *p* and two largest *d* helium exponents of B61 were optimized by minimizing the FCI correlation energy of helium in the triplet state using the helium part of our dimer basis set. In the same way we optimized the four largest *p* and three largest *d* helium exponents of B106. The remaining *p* exponents on helium and all *p* exponents on the hydrogen atom were determined by optimizing the C_6 dispersion constant calculated from the formula[57]

$$C_6 = -6 \sum_{s \neq 0} \sum_{u \neq 0} \frac{|\langle \phi_0^{\mathrm{A}} | z_1 + z_2 | \phi_s^{\mathrm{A}} \rangle|^2 \, |\langle \phi_0^{\mathrm{B}} | z_3 | \phi_u^{\mathrm{B}} \rangle|^2}{\omega_s^{\mathrm{A}} + \omega_u^{\mathrm{B}}}, \qquad (43)$$

where ϕ_s^{A} are the FCI wave functions for the triplet states of helium and ϕ_u^{B} are hydrogen atom wave functions computed using the helium and hydrogen parts, respectively, of the original atomic basis set, while ω_s^{A} and ω_u^{B} are the corresponding excitation energies. The *s* exponents were kept fixed during the optimizations.

TABLE I
Optimized exponents of the p, d, and f orbitals used in this work

base	Atom	Orbital	Optimized exponents
B61	He	5p	0.01838, 0.04287, 0.1164, 0.4351, 1.309
		3d	0.0281, 0.211, 0.777
	H	3p	0.06764, 0.1895, 0.7176
		2d	0.0669, 0.201
B106	He	7p	0.00701, 0.01861, 0.03933, 0.09039, 0.3039, 0.6962, 2.336
		5d	0.0180, 0.0435, 0.184, 0.578, 1.34
		2f	0.018, 0.044
	H	4p	0.05742, 0.1401, 0.3948, 1.563
		3d	0.0539, 0.130, 0.385
		1f	0.081

The remaining *d* exponents on helium and all *d* exponents on hydrogen were determined in a similar way by optimizing the dispersion constant C_8 without changing the values of *s* and *p* exponents determined in previous steps. Finally, the *f* exponents were determined by optimizing the dispersion constant C_{10} keeping the *s*, *p*, and *d* exponents fixed. The C_8 and C_{10} constants were computed at the FCI level from the formulas analogous to Eq. (*43*), see ref.[57]

The optimization of the C_6, C_8, and C_{10} constants was performed using a code written specifically for this task, making use of the multipole moment integrals calculated using the ATMOL package[58] and transformed to the Hartree–Fock basis by means of a properly modified transformation program from the SAPT2002 suite of codes[29]. The obtained values of dispersion constants, presented in Table II, compare well with the literature results of Spelsberg and Meyer[59].

Atomic integrals and the HF orbitals for helium were obtained using the ATMOL package[58]. The four-index transformation of atomic integrals was performed using a modification of the transformation program from the SAPT2002 package[29]. Since the limit of the converged perturbation series was sensitive to the accuracy of the diagonalization of H_B, it was necessary to perform this diagonalization with a very high precision. Specifically, to obtain good agreement with the FCI interaction energy all off-diagonal elements of H_B had to be smaller than 10^{-13}.

As our basis set consisted of Gaussian-type orbitals and the function used to regularize the Coulomb singularities was also Gaussian, the one-electron integrals with the potential v_p could be easily obtained using the well-known fact that the product of two *s* Gaussian functions is also an *s* Gaussian function located on the line joining the centers of the multiplied functions. When one of the Gaussian functions has an angular factor, this angular factor has to be shifted to the new center, which can be easily done using the well-known translation formula for solid spherical harmonics[60].

TABLE II

Values of the C_6, C_8, and C_{10} coefficients for the 1s2s triplet-state helium–ground-state hydrogen atom interaction obtained using bases B61 and B106

Basis	$C_6 \times 10^1$	$C_8 \times 10^3$	$C_{10} \times 10^5$
B61	–8.786	–5.099	
B106	–8.791	–5.200	–4.198
Ref.[59]	–8.784	–5.181	–4.165

FCI and High-Order SAPT Calculations

To obtain the zeroth-order function and energy for helium and to calculate the reference supermolecular interaction energy for the lowest $^4\Sigma^+$ state of HeH, we performed the FCI calculations in the spaces $\mathcal{H}_A$ and $\mathcal{H}_A \otimes \mathcal{H}_B$, respectively. For helium we used the conventional Davidson methods[61] as coded by Duch[62]. For the lowest quartet state of HeH we used a symmetry-adapted Davidson procedure described in ref.[30] In this modification of the Davidson method, the trial functions for computing the energy in a given iteration are symmetry projected onto the subspace of appropriate permutational symmetry, in our case with the antisymmetrizer $\mathcal{A}$. This projection is necessary since the basis set in $\mathcal{H}_A \otimes \mathcal{H}_B$ is not adapted to the full symmetry of the Hamiltonian, and the conventional Davidson iterations do not conserve the symmetry of functions obtained in preceding iterations[30]. In the case of the helium atom, the initial guess for the iterations was a unit vector in the two-electron basis set, chosen such that the diagonal element of helium Hamiltonian had the lowest value. In the case of HeH, the starting point was a vector of the coefficients specifying the function $\mathcal{A}\phi_A\phi_B$. The termination condition was that the norm of the residual vector had the value of 10^{-14} for helium calculations and 10^{-10} for dimer calculations.

The perturbation energies and wave functions were obtained by solving the systems of linear equations resulting from converting the formulas of the second and third Chapters of the paper into matrix form. These equations have the form $\boldsymbol{Mx} = \boldsymbol{b}$, where $\boldsymbol{M}$ is a diagonal block of the matrix of the operator $H_A + H_B - E^{(0)} + P_0$, $\boldsymbol{x}$ is the vector of appropriate coefficients defining a wave function correction, and $\boldsymbol{b}$ is the right-hand side vector characteristic of a given SAPT theory. The preconditioned conjugate gradient method[63] was used to solve all linear equations. This means that instead of the equation $\boldsymbol{Mx} = \boldsymbol{b}$, an equivalent system of linear equations

$$(\boldsymbol{D}^{-1/2}\boldsymbol{M}\boldsymbol{D}^{-1/2})(\boldsymbol{D}^{1/2}\boldsymbol{x}) = \boldsymbol{D}^{-1/2}\boldsymbol{b} \qquad (44)$$

was solved, where $\boldsymbol{D}$ is a diagonal matrix whose diagonal elements are the same as in $\boldsymbol{M}$. The Davidson and the conjugate gradient iterations require an efficient implementation of the multiplication of the matrices of operators H_0, V, V_p, V_t, and $\mathcal{A}$ by a given vector. These multiplications were implemented in such a way that the sparseness of matrices was fully exploited.

RESULTS AND DISCUSSION

Results of FCI Calculations

The results of FCI calculations of the interaction energy in the $^4\Sigma^+$ state of HeH are presented in Table III, while Fig. 2 shows the FCI potential energy curve obtained with our largest basis set. It is seen that this state has a very shallow van der Waals minimum at the distance of approximately 12.5 bohr. The depth D_e of this minimum amounts to only 18.6 μhartree (or 4.08 cm^{-1}) when the two largest bases are used. It is interesting to note that the midbond functions are very effective at the minimum and at shorter distances. In this range 22 midbond functions give more energy lowering than 45 dispersion optimized functions located at the atomic positions.

TABLE III
The FCI interaction energy for lowest $^4\Sigma^+$ state of HeH obtained using bases B61, B61+22b and B106. The energy unit is 1 μhartree

R	B61	B61+22b	B106
10.0	63.60821	48.82623	49.90129
10.5	23.41081	12.66392	13.37579
11.0	1.34175	–6.38659	–5.98361
11.5	–9.78497	–15.30847	–15.11469
12.0	–14.54479	–18.48362	–18.41146
12.5	–15.77115	–18.58103	–18.57218
13.0	–15.16788	–17.17602	–17.19734
13.5	–13.72563	–15.16418	–15.19883
14.0	–11.99659	–13.02956	–13.06966
14.5	–10.27076	–11.01405	–11.05607
15.0	–8.68617	–9.22188	–9.26421
16.0	–6.10891	–6.38801	–6.42851
18.0	–3.02426	–3.10087	–3.13119
20.0	–1.57397	–1.59567	–1.61369
22.0	–0.86973	–0.87616	–0.88572
24.0	–0.50703	–0.50903	–0.51396
26.0	–0.30930	–0.30996	–0.31253
28.0	–0.19606	–0.19629	–0.19766

We found that this very shallow minimum does support bound rovibrational levels (in nonrelativistic approximation). In fact all possible stable isotopic varieties are bound and the heaviest ones support even a $J = 1$ rotationally excited level. This may be viewed as surprising since the ground, $X^2\Sigma^+$ state of HeH, which exhibits somewhat deeper van der Waals well, remains clearly unbound, even for the heaviest stable isotopes[64]. All 9 levels (neglecting the spin-orbit and spin-rotation splittings) found by us, marked on Fig. 2 and listed in Table IV, lie very close to the dissociation threshold. The highest one makes a remarkably long-range molecule. With

TABLE IV
The energies of the bound levels. The employed potential was fitted to the FCI interaction energies calculated with basis B106. The energy unit is 1 cm^{-1}

	$J = 0$	$J = 1$
^{3}HeH	–0.006958	–
^{4}HeH	–0.01871	–
^{3}HeD	–0.2044	–
^{4}HeD	–0.2764	–0.01538
^{3}HeT	–0.3671	–0.1014
^{4}HeT	–0.4770	–0.2191

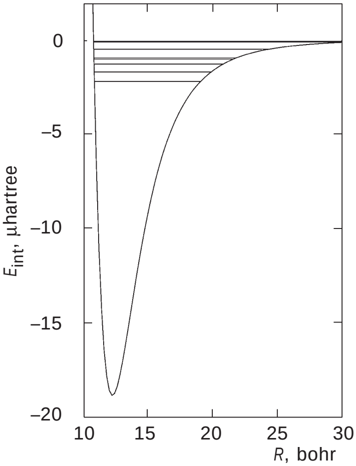

FIG. 2
The supermolecular FCI interaction potential of the lowest $^4\Sigma^+$ state of HeH and the bound states supported by this potential for all possible isotopic varieties of HeH. The basis used in calculations was B106

an average interatomic distance of about 35 Å, this molecule is almost as large as the helium dimer[65,66]. To our knowledge this is the first report of bound levels for the lowest quartet of HeH (some higher excited quartet states of HeH appear to be chemically bound[67] and can be expected to support many rovibrational levels).

Convergence of Nonregularized SAPT Expansions

The results of the large-order SAPT calculations using non-regularized expansions are shown in Table V and in Fig. 3. The percentage errors listed in Table V are defined as

$$\delta(n) = 100\% \times \left(\sum_{k=1}^{n} \mathcal{E}^{(k)}_{\mathrm{SAPT}} - \mathcal{E}_{\mathrm{FCI}}\right) / \mathcal{E}_{\mathrm{FCI}} \; . \tag{45}$$

TABLE V
Percentage error δ(*n*), *cf*. Eq. (*45*), resulting from summing the nonregularized SAPT expansions through the *n*-th order. The basis B61+22b was used and the interatomic distance was 12.5 bohr

n	SRS	ELHAV	SAM	JK
1	–202.13092	–202.13092	–202.13092	–202.13092
2	–9.00545	–83.21122	–83.21207	–9.00545
3	–14.20413	–35.85221	–35.85394	–5.11364
4	–9.75615	–15.91323	–15.91309	–2.70588
5	–8.74017	–7.22648	–7.22435	–1.41098
6	–7.15589	–3.34788	–3.34464	–0.73782
7	–6.08711	–1.58092	–1.57742	–0.38951
8	–5.10323	–0.76108	–0.75785	–0.20814
9	–4.31473	–0.37380	–0.37109	–0.11266
10	–3.64174	–0.18746	–0.18532	–0.06175
15	–1.60845	–0.00821	–0.00778	–0.00355
20	–0.75535	–0.00056	–0.00049	–0.00024
25	–0.44644	–0.00005	–0.00004	–0.00002
30	–0.65426	0.00000	0.00000	0.00000
35	–2.56462			
40	–12.91990			

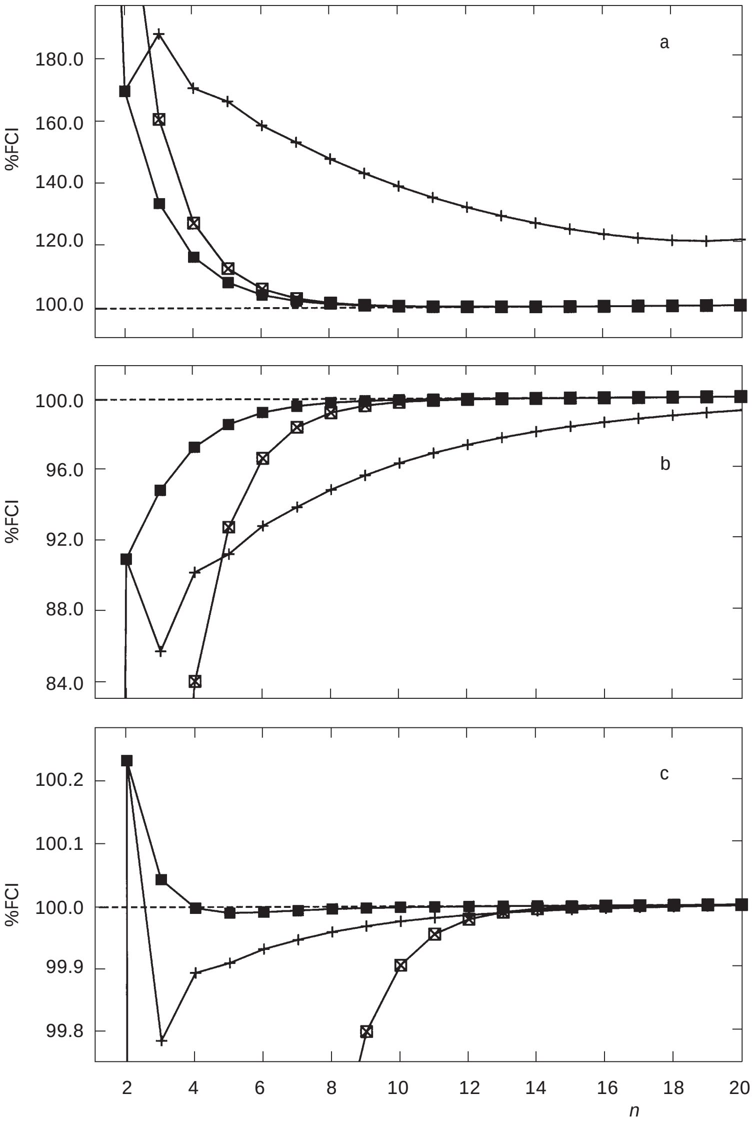

FIG. 3
Percentage of the FCI interaction energy recovered through the *n*-th order of the SRS (+), ELHAV (×), SAM (□), and JK (■) theory. The basis B61+22b was used and the distance was 10.0 (a), 12.5 (b), 18.0 bohr (c)

The perturbation calculations were carried out using the bases B61, B61+22b, and B106 and we found only small differences in the convergence rate when the basis set was improving. The general trend was that in a larger bases the convergent methods (ELHAV, AM, JK) converged slightly better, and the divergent methods (RS and SRS) diverged slightly worse. The latter behavior can be rationalized since in larger basis sets the continuum of the doublet permutational symmetry is described better and it is the interaction with this continuum that causes the divergence of the RS and SRS series.

The data from Table V and Fig. 3 show that, as expected, the SRS series diverges in high orders, while the ELHAV, SAM, and JK expansions are convergent, despite the continuum of intruder states shown in Fig. 1. For the ELHAV and JK expansions this observation is in agreement with the results found in similar calculations[31] for the LiH molecule. It is interesting to observe that the ELHAV and SAM expansions give practically identical results. Similar observation was also recently made in ref.[54] In low orders, the convergence of the ELHAV and SAM expansions is very poor, especially at large R. This is understandable in view of the well-known incorrect asymptotic behavior of the second- and higher-order energies in these methods[49,50]. We found that at large R the second-order ELHAV or SAM energies reproduce only about 55% of the exact C_6R^{-6} asymptotics of the interaction energy (due entirely to the dispersion interaction in this case). The JK method, in agreement with the results of ref.[31], shows very good convergence both in low and high orders. The good low-order convergence is obviously due to the fact that 100% of the dispersion energy is recovered through the second order. Figure 3 shows that at smaller interatomic distances the divergence of the SRS method manifests itself in lower orders. The convergent methods converge also somewhat slower at smaller R, especially in low orders, but in large orders the convergence rate appears to be almost independent of R.

Convergence of Regularized SAPT Expansions

The η dependence of the ground-state energy and of the ionization threshold of the regularized Hamiltonian $H_0 + V_p(\eta)$ are plotted in Fig. 4 (we assumed that $\eta_A = \eta_B = \eta$) for $R = 12.5$ bohr. This figure shows that for a wide range of η (note the logarithmic scale on the η axis) the continuous spectrum of $H_0 + V_p(\eta)$ is moved far above the ground-state energy of H_0 (equal to –2.675 hartree). However, at η equal to a critical value $\eta_c = 2.7$ the ground-state wave function $\psi_p(\eta)$ undergoes a qualitative change and looses its similarity to the unperturbed function ϕ_0. The corresponding eigenvalue $E_p(\eta)$ shows an abrupt downward bend at the same value of η. Thus, only the values of η smaller than 2.7 can be used in the perturbation expansion of the interaction energy. We found that the critical value of the regularization parameter η_c depends very weakly on R and is close to 2.7 for the distances of the van der Waals well and larger. Asymptotically, at infinite R, η_c can be easily computed from monomer properties only. We found that this asymptotic value is equal to 2.7, *i.e.*, is the same as for $R = 12.5$ bohr. It should be mentioned that η_c does not show significant basis set dependence. The value of $\eta_c = 2.7$ was obtained with all three bases used by us.

The possible infinite-order limit of the R-RS expansion (given by Eq. (*31*) when $\mathcal{A} = 1$ and $\lambda = 1$) and of the R-SRS expansion (given by Eq. (*31*) when $\lambda = 1$), computed for different values of R assuming $\eta = 2.5$ are compared in Table VI with the corresponding FCI interaction energies. The result of this comparison is rather disappointing. For the considered system, the infinite-order R-SRS theory cannot provide an acceptable approximation to the interaction energy. Although, as shown in Fig. 5, the R-SRS series converges very fast for $\eta < \eta_c$, its limit differs by about 15% from the exact interaction energy at $R = 12.5$ bohr. This can be contrasted with the similar limit for the interaction of two ground-state hydrogen atoms[42], which differed by less than 2% from the exact result at the van der Waals minimum distance

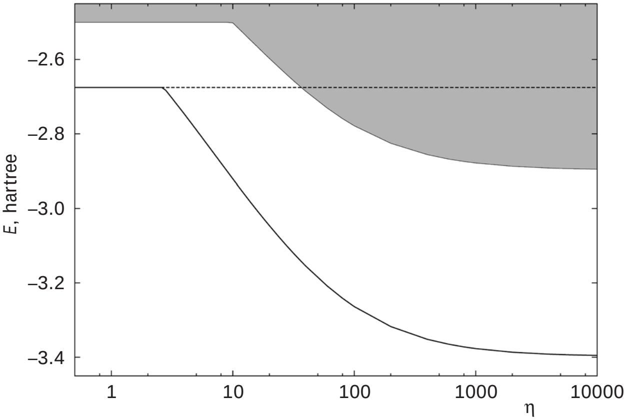

FIG. 4

The ground state and the ionization threshold of the regularized Hamiltonian $H(\eta) = H_0 + V_p(\eta)$ as a function of the parameter η. The dashed line represents the infinite-order R-SRS energy $E_{\text{R-SRS}}(1)$, *cf.* Eq. (*31*), which is undistinguishable at this energy scale from the FCI energy. The basis B61 was used and the interatomic distance 12.5 bohr was assumed of 8 bohr. At larger distances, the infinite-order R-SRS energy becomes more accurate since it has the same large-*R* asymptotics as the exact energy. However, the exponentially vanishing exchange contribution to the interaction energy, which in this case can be defined as the difference between the FCI and the infinite-order R-RS energies, is not too well reproduced at large *R*. The numbers displayed in the last column of Table VI show that this exchange contribution is reproduced with a relative error of about 10% at the minimum and that this relative error decreases very slowly with *R* (it is not clear from our data if this relative error vanishes when *R* increases to infinity).

The above discussion shows that the singular part V_t of the perturbation V cannot be neglected if the accuracy of a few percent or less is required. The convergence of the R-SAM theory, the ZI theory of Adams, and the SNC-P1 expansion, which include the effect of the V_t operator, is shown in Table VII and in Fig. 6. It is seen that despite the singular nature of V_t, all three expansions converge fast. This shows that the operator $\mathcal{A}V_t$ is indeed a much weaker perturbation than V_t itself. As V_t has a short-range character, all perturbation energies in the regularized expansions considered in this work have the correct asymptotic behavior, consistent with the theory of Ahlrichs[45]. Somewhat disappointingly we do not see a significant advantage the ZI theory of Adams might have over the simpler R-SAM treatment.

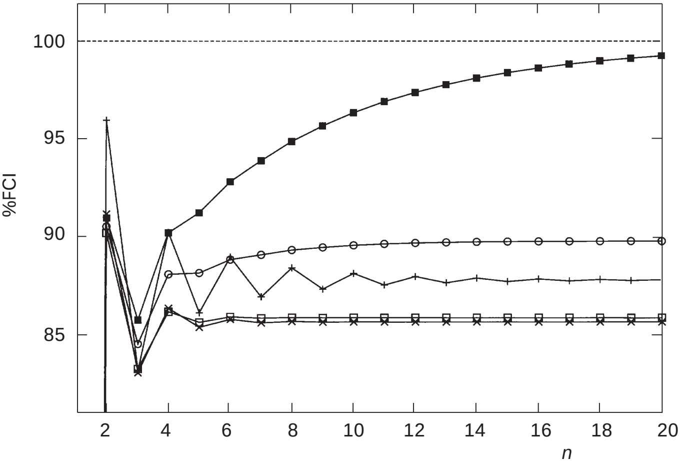

FIG. 5

Percentage of the FCI interaction energy recovered through the *n*-th order of the SRS theory (■) and the R-SRS theory with different values of the regularization parameter η: 0.4 (+), 1.0 (×), 2.5 (□), and 10.0 (○). The basis B61+22b was used and the distance was 12.5 bohr

The plots presented in Fig. 6 show that the SNC-P1 approach provides results of practically the same accuracy as the R-SAM or ZI methods. This is gratifying since the SNC-P1 regularization is computationally simplest (it does not require any new integrals) and is independent of the somewhat arbitrary choice of the regularization parameter η. It should be noted, however, that the SNC-P1 method cannot be generalized in an obvious way to polyatomic dimers.

We also tested the role of the offset parameter *D* in the R-SAM theory. We found that for the considered dimer and the range of interatomic distances the R-SAM perturbation energies change insignificantly if this parameter is set equal to zero. We decided to keep it to preserve the consistency with Adams's formulation[43].

TABLE VI

The infinite-order limits of the R-RS and the R-SRS theory as functions of the interatomic distance *R* computed with basis B61+22b. The regularization parameter was fixed at η = 2.5. The energy unit is 1 μhartree

R	R-RS	R-SRS	FCI	Δ[a]
10.0	–227.86949	92.50762	48.82623	15.79
10.5	–158.51431	37.52599	12.66392	14.52
11.0	–111.63110	7.77912	–6.38659	13.46
11.5	–79.64322	–7.23588	–15.30847	12.55
12.0	–57.60281	–13.88405	–18.48362	11.76
12.5	–42.25281	–15.96082	–18.58103	11.07
13.0	–31.43713	–15.68347	–17.17602	10.47
13.5	–23.72114	–14.31381	–15.16418	9.94
14.0	–18.14477	–12.54480	–13.02956	9.48
14.5	–14.06120	–10.73745	–11.01405	9.08
15.0	–11.03117	–9.06386	–9.22188	8.73
16.0	–7.02027	–6.33626	–6.38801	8.19
18.0	–3.17596	–3.09526	–3.10087	7.47
20.0	–1.60438	–1.59506	–1.59567	7.00
22.0	–0.87715	–0.87610	–0.87616	6.59

[a] Calculated using formula Δ = 100% × |R-SRS – FCI|/|R-RS – FCI|.

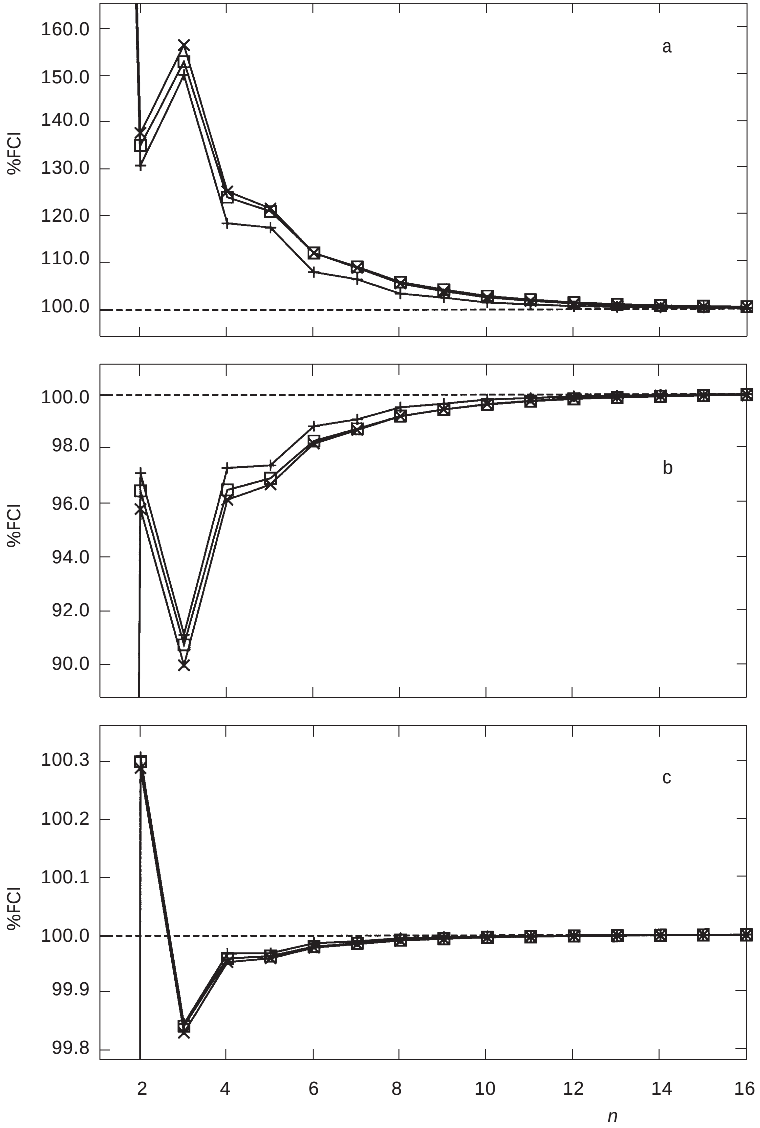

FIG. 6

Percentage of the FCI interaction energy recovered through the *n*-th order of the R-SAM (+), ZI (×), and SNC-P1 (☐) theory. In the R-SAM and ZI theories the regularization parameter was η = 1.0. The basis B61+22b was used and the distance was 10.0 (a), 12.5 (b), 18.0 bohr (c)

TABLE VII
Percentage error δ(*n*), *cf*. Eq. (*45*), resulting from summing the regularized SAPT expansions through the *n*-th order. The basis B61+22b was used, the regularization parameter was η = 1.0, and the interatomic distance was 12.5 bohr

n	R-SAM	ZI	SNC-P1
1	–202.13092	–203.94561	–202.13092
2	–2.87821	–4.19592	–3.52698
3	–8.83065	–9.96677	–9.20189
4	–2.69129	–3.85397	–3.48907
5	–2.59956	–3.29154	–3.06905
6	–1.14016	–1.79396	–1.69241
7	–0.89274	–1.28666	–1.24384
8	–0.45103	–0.78136	–0.77057
9	–0.32172	–0.53025	–0.53488
10	–0.17670	–0.33752	–0.34787
15	–0.01764	–0.04314	–0.04913
20	–0.00153	–0.00583	–0.00722
25	–0.00005	–0.00080	–0.00106
30	0.00003	–0.00010	–0.00014
35	0.00001	–0.00001	–0.00001
40	0.00000	0.00000	0.00000

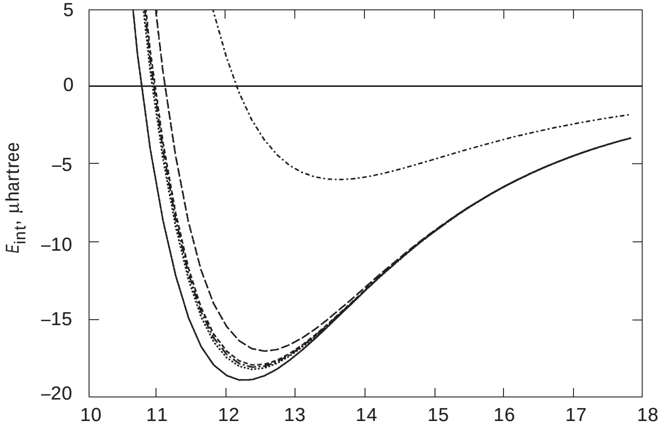

Fig. 7
Comparison of the interaction energy recovered through the second order for different SAPT theories with the FCI interaction energy as a function of the interatomic distance *R*. In the R-SAM and ZI theories the regularization parameter was η = 1.0. The basis B61+22b was used in calculations. FCI (——), ELHAV (- · - - · -), JK (– – – –), R-SAM (· · · ·), ZI (- - - -), and SNC-P1 (– · – · –)

In Fig. 7 we show how accurate approximation is obtained when the perturbation techniques discussed in this work are applied through the second order. Except for the ELHAV (or SAM) theory all second-order approaches provide qualitatively similar results. It is clear from this figure, however, that to obtain a very high, spectroscopic accuracy, the effects of the third and higher orders must be taken into account. In view of their demonstrated convergence, the expansions considered in this work can be used to systematically include these higher-order effects.

CONCLUSIONS AND OUTLOOK

The conclusions of our investigation can be summarized as follows:

– The coupling with the continuum of physical states of different permutational symmetry leads to the divergence of the RS and SRS expansions for the lowest quartet state of HeH.

– The conventional SAPT expansions based on forcing the proper symmetry in the equations for the wave function (the ELHAV and JK expansions) are convergent in this case, albeit the ELHAV expansion converges very slowly in low orders due to an incorrect asymptotic behavior of the second- and higher-order corrections.

– The original and symmetrized Amos–Musher expansions are convergent in high orders. This confirms the hypothesis of Adams that the symmetrized interaction operator $\mathcal{A}V$ is a much weaker perturbation than the operator V itself.

– The symmetrized version of the Amos–Musher theory leads to results which are practically identical with those given by the ELHAV theory.

– The regularized SRS theory converges very fast but its infinite-order limit does not represent a sufficiently good approximation to the interaction energy.

– The regularized SRS theory can be corrected by including the short-range, singular part of the perturbation. This can be achieved using the idea of the symmetrized Amos–Musher theory. The resulting perturbation expansions involving the Gaussian, or a smeared nuclear charge regularization exhibit very fast convergence and provide good results in low order.

One may ask, of course, if the conclusions we arrived at can be transferred to larger systems. We believe that the lowest quartet state of HeH, unlike the two lowest states of H_2 or the ground state of He_2, is a system for which all essential complications plaguing the SAPT treatment of many-electron systems are present. Therefore, we expect that the main conclusions of our investigation can transfer to larger systems. In fact, calculations performed for the interaction involving the ground-state lithium and hydrogen atoms (for this system the ground-state of the dimer is submerged in a Pauli forbidden continuum) lead to similar conclusions[54] and we believe that the converged SAPT expansions considered in the present work and in ref.[54] form a basis for a systematic extension of SAPT beyond the conventional second order. Applications to larger systems would, of course, require some approximate handling of the intramonomer correlation problem using, *e.g.*, the ideas of the coupled cluster and/or many-body perturbation theory. Work in this direction is in progress in our laboratory.

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