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Degenerate symmetry-adapted perturbation theory of weak interactions between closed- and open-shell monomers: application to Rydberg states of helium hydride

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Abstract. Symmetry-adapted perturbation theory is extended to the (quasi) degenerate, open-shell case. The new formalism is tested in calculations of the interaction energies for a helium atom in the ground state interacting with an excited hydrogen atom. It is shown that the method gives satisfactory results if the coupling with higher Rydberg states of the dimer is small, as is the case for the $A^2\Sigma^+$, $B^2\Pi$, $E^2\Pi$, $3^2\Pi$, and $1^2\Delta$ states of HeH. For the $C^2\Sigma^+$ state convergence of the method is very slow, but it can be improved by including the $n = 3$ states in the model space.

Key words: Symmetry-adapted perturbation theory – Open-shell dimers – Weak interatomic interactions – Rydberg states – Helium hydride

1 Introduction

Intermolecular interactions involving closed- and open-shell monomers are nowadays a subject of growing interest (see, for instance, Refs. [1, 2] for a review of experimental activity in this area). Potential energy surfaces for weakly bound open-shell complexes can be computed using the supermolecular method [3]. However, straightforward applications of this conceptually simple approach are far from trivial. Size-consistent methods, such as conventional single-reference many-body perturbation theory [4] or the coupled-cluster method [5, 6], can only be applied when the unrestricted Hartree-Fock determinant is used as the reference state. Consequently, the correlated wave functions for dimers are not pure spin functions, and it is difficult to estimate a priori how spin contamination affects computed interaction energies [7]. On the other hand, multireference coupled-cluster methods that are size-consistent and do not break the spin symmetry are not sufficiently

developed [6] to be routinely applied in studies of weak intermolecular complexes.

Direct, intermolecular perturbation theory studies of interaction energies in open-shell complexes are scarce [8]. The pioneering work in this field was performed by Chalasinski and Szalewicz [9] who generalized the perturbation theories developed earlier by Hirschfelder [10], van der Avoird [11], Murrell and Shaw [12] and, Musher and Amos [13] to degenerate systems. Representing the interaction energy as a power series in the formal strength parameter λ Chalasinski and Szalewicz found that for the $H\cdots H^+$ test system the perturbation expansions studied by them were divergent for $\lambda = 1$, i.e., for the physical value of the parameter λ . The divergence also persisted at large internuclear distances, R , although the low-order results were remarkably accurate at the van der Waals minimum region. One can expect that the techniques of model spaces and wave operators [14], characteristic of recent developments in degenerate and quasidegenerate perturbation theory, may lead to better convergence than the straightforward power series expansion considered by Chalasinski and Szalewicz.

The most difficult problem in the perturbation theory of intermolecular interactions is the necessity to account for the exchange energy, i.e., for that part of the interaction energy which arises from the resonance tunneling of electrons between the interacting monomers. In the conventional Rayleigh-Schrödinger perturbation approach to intermolecular interactions, usually referred to as the polarization approximation [8], one starts from the zeroth-order wave function which is not antisymmetric with respect to permutations of electrons between monomers. Various methods, referred to collectively as symmetry-adapted perturbation theory (SAPT), were proposed to correct this deficiency and to force the proper symmetry on the perturbed wave function [15]. For an insightful presentation of the mathematical foundations of SAPT, including a discussion of still unresolved problems, we refer the reader to the series of papers published recently by Adams [16–19]. Fortunately, the simplest approach, referred to as symmetri-

zed Rayleigh-Schrödinger perturbation theory (SRS) [20, 21], appears to be sufficiently accurate to predict the interaction energies with an error of a few percent [22–24]. At present, interactions between closed-shell systems can routinely be studied by the many-body version of SAPT which is applicable to many-electron, polyatomic dimers (see Ref. [8] for a review). The potential energy surfaces obtained by SAPT were successfully applied to explain the experimental infrared spectra [25], scattering processes [26], and bulk properties [27] of numerous van der Waals dimers (see Refs. [28, 29] for recent reviews). Recently, the SAPT approach has been generalized to nonadditive interactions in trimers [30] and to collision-induced properties [31].

Since the SAPT approach has been successfully applied to describe intermolecular interactions and properties of closed-shell systems, it is interesting to investigate if a similar approach can work for complexes involving open-shell monomers. In this work we present a generalization of the SAPT approach to degenerate and quasidegenerate situations. Our approach is based on general localization ideas introduced earlier by Adams [32], Chipman [33], and Klein [34]. The applicability of this new method is tested on the simple example of a ground-state helium atom interacting with an excited hydrogen atom, i.e., on the Rydberg states of the HeH molecule. For this system full configuration interaction (FCI) calculations with reasonably large basis sets can be performed, so comparison of the finite-order perturbation theory results with the exact infinite-order limits is possible. The excited states of HeH are of considerable current experimental and theoretical interest. Since the development of new experimental techniques for the detection of the excimer states [35] a large number of theoretical and experimental works considering various aspects of the Rydberg states of the HeH system appeared in the literature [35–38].

2 Theory

To simplify the notation we shall consider the particular case of a two-electron system A in a nondegenerate state interacting with a one-electron system B in an excited, degenerate state. In actual applications A will be a helium atom in the ground state and B an excited hydrogen atom. The general idea of our method is, however, applicable to larger systems, although the details concerning the permutational symmetry of the many-electron wave function will differ and will lead to more complicated system-specific equations.

We use the usual partitioning of the total Born-Oppenheimer Hamiltonian H into an unperturbed part being the sum of monomer Hamiltonians, $H_0 = H_A + H_B$, and a perturbation operator $V = H - H_0$. The eigenfunctions of the unperturbed operator H_0 are given by

$$\phi_{0k}^{(0)} = \Phi(\mathbf{r}_1, \mathbf{r}_2)\chi_k(\mathbf{r}_3) , \quad (1)$$

where $\Phi(\mathbf{r}_1, \mathbf{r}_2)$ is the spatial part of the ground-state wave function of the helium atom and $\chi_k(\mathbf{r}_3)$ is a

hydrogen orbital with an index k collecting all three quantum numbers n, l , and m . The orbitals $\chi_k(\mathbf{r}_3)$ used in the construction of the zeroth-order approximation to the wave functions form the so-called active set. The functions $\phi_{0k}^{(0)}$ correspond to the eigenvalue $E_k^{(0)} = E_{\text{He},0} + E_{\text{H},k}$.

For the excited ($n = 2$) hydrogen atom the simplest active set consists of four orbitals: $2s, 2p_z, 2p_x$, and $2p_y$. The formalism presented below is valid for a general, quasidegenerate case, so we do not have to assume that all $\phi_{0,k}^{(0)}$ functions correspond to the same eigenvalue of H_0 . Therefore, higher excited χ_k orbitals can be added to the active set, if necessary. The number of elements of this set will be denoted by D . It should be noted that for low-lying excited states of HeH we do not have to consider excited states of the He atom, since the excitation energy of the latter (≈ 0.75 hartree) is larger than the first ionization energy of the hydrogen atom (0.5 hartree). However, if we take an argon atom instead of helium, some excited states of argon should also be taken into account [39].

The symmetry operations of the total Hamiltonian H form the group $S_3 \times C_{\infty v}$, i.e., the product of the symmetric group S_3 and the axial symmetry group $C_{\infty v}$. The linear space spanned by the zeroth-order approximations to the exact wave functions (the so-called model space) should be invariant under this group. Obviously, the space spanned by $\phi_{0k}^{(0)}, k = 1, \dots, D$, does not meet this requirement, since the functions $\phi_{0k}^{(0)}$ transform according to the $[2] \times [1]$ irrep of $S_2 \times S_1$ and do not carry a representation of the permutation group S_3 . To assure proper symmetry properties of the model space under S_3 permutations, all functions of the type $\pi\phi_{0k}^{(0)}, \pi \in S_3$, should be included. Since

$$P_{12}\phi_{0k}^{(0)} = \phi_{0k}^{(0)} , \quad (2)$$

it is sufficient to include the functions $\phi_{0k}^{(0)}, \phi_{1k}^{(0)}$, and $\phi_{2k}^{(0)}$, where

$$\phi_{1k}^{(0)} \stackrel{\text{def}}{=} P_{13}\phi_{0k}^{(0)} , \quad (3)$$

$$\phi_{2k}^{(0)} \stackrel{\text{def}}{=} P_{23}\phi_{0k}^{(0)} . \quad (4)$$

The linearly independent functions $\phi_{\alpha k}^{(0)}, \alpha = 0, 1, 2$, correspond to the three possible localizations of electrons 1, 2, and 3 on A and B. The model space invariant under S_3 , spanned by $M = 3D$ functions $\phi_{\alpha k}^{(0)}, \alpha = 0, 1, 2, k = 1, \dots, D$, will be denoted by \mathcal{M}_0 . The projection operator on \mathcal{M}_0 will be denoted by P , whereas P_α shall denote the operator projecting on the subspace with specific localization of electrons on A and B,

$$P_\alpha = \sum_k |\phi_{\alpha k}^{(0)}\rangle\langle\phi_{\alpha k}^{(0)}| . \quad (5)$$

The summation in Eq. (5) runs over all orbitals from the active set. Note that the operators P_α project on subspaces which are not mutually orthogonal so P is not equal to the sum of the P_α s. The wave functions $\phi_{1k}^{(0)}$ and $\phi_{2k}^{(0)}$ are eigenfunctions of the unperturbed Hamiltonians with appropriately permuted electronic coordinates $H_1 \stackrel{\text{def}}{=} P_{13}H_0P_{13}$ and $H_2 \stackrel{\text{def}}{=} P_{23}H_0P_{23}$, respectively,

$$H_\alpha \phi_{\alpha k}^{(0)} = E_k^{(0)} \phi_{\alpha k}^{(0)} . \quad (6)$$

For each H_α , a perturbation operator V_α is defined as the difference $V_\alpha = H - H_\alpha$.

The target space \mathcal{M} , associated with the model space \mathcal{M}_0 , consists of all (physical and nonphysical) eigenfunctions of the total Hamiltonian H which correspond – in the asymptotic limit of large interatomic distance R – to the energy $E_k^{(0)}$ (or a given range of unperturbed energies). Any set of M functions $\phi_{\alpha k}$ spanning the target space \mathcal{M} satisfies the system of equations

$$(H - E_k^{(0)})\phi_{\alpha k} = \sum_\beta \sum_l Q_{\alpha k}^{\beta l} \phi_{\beta l} . \quad (7)$$

Once the coefficients $Q_{\alpha k}^{\beta l}$ are known, the target space eigenvalues of the Hamiltonian can be obtained by diagonalization of the matrix \mathbf{Q} defined by

$$\tilde{Q}_{\alpha k}^{\beta l} = Q_{\alpha k}^{\beta l} + E_k^{(0)} \delta_{kl} \delta_{\alpha\beta} . \quad (8)$$

$\tilde{Q}_{\alpha k}^{\beta l}$ is the matrix representation of H in the invariant subspace spanned by the non-orthogonal basis $\phi_{\alpha k}$. The eigenvectors $\tilde{\mathbf{d}}_i$

$$\tilde{\mathbf{Q}}\tilde{\mathbf{d}}_i = E_i \tilde{\mathbf{d}}_i \quad (9)$$

define the target space eigenfunctions ψ_i of H in terms of the basis functions $\phi_{\alpha k}$,

$$\psi_i = \sum_\alpha \sum_k d_i^{\alpha k} \phi_{\alpha k} . \quad (10)$$

If all unperturbed wave functions correspond to the same energy, the diagonalization of \mathbf{Q} gives the required interaction energies directly. Thus, the matrix \mathbf{Q} plays a similar role to that of the effective interaction matrix in conventional degenerate perturbation theory [14].

The functions $\phi_{\alpha k}$ satisfying Eq. (7) will be referred to generally as the primitive [40] or localized [32, 41] wave functions (note that the exact eigenfunctions of H also belong to the class of primitive functions). They transform according to the induced representation $([2] \times [1]) \uparrow S_3 = [3] + [2, 1]$ of the group S_3 . The exact, “delocalized” eigenfunctions ψ_i are of definite permutational symmetry and transform according to the [3] or [2, 1] irreps of S_3 . The functions belonging to the two-dimensional irrep [2, 1] appear in degenerate pairs and, after multiplication by appropriate spin functions, can be used to construct a fully antisymmetric spin-dependent wave function. The functions belonging to the [3] irrep cannot be used to build an antisymmetric wave function and are discarded.

Obviously, the functions $\phi_{\alpha k}$, and hence also the coefficients $Q_{\alpha k}^{\beta l}$, are not uniquely defined by Eq. (7). To specify them uniquely one has to impose some additional constraints referred to as localization conditions. These localization conditions should be chosen in such a way that $\phi_{\alpha k}$ is as similar as possible to $\phi_{\alpha k}^{(0)}$; in particular, these two wave functions must correspond to the same localization of electrons at interacting monomers. One can expect that $\phi_{\alpha k}$ can then be obtained by means of perturbation theory or an iterative procedure utilizing $\phi_{\alpha k}^{(0)}$ as the zeroth-order approximation. To define spe-

cific localization conditions it is convenient to introduce the wave operator U (define on \mathcal{M}_0) that transforms the unperturbed wave function $\phi_{\alpha k}^{(0)}$ into the exact primitive function $\phi_{\alpha k}$:

$$U\phi_{\alpha k}^{(0)} = \phi_{\alpha k} . \quad (11)$$

In the present study we shall consider three localization conditions, referred to for historical reasons [42] as the Bloch [34, 43], Hirschfelder-Silbey (HS) [44], and Kato [33, 45] localizations.

2.1 Bloch localization condition

The wave operator corresponding to Bloch localization [34] is defined by the equations

$$P_\alpha U P_\beta = P_\alpha P_\beta, \quad \text{for } \alpha, \beta = 0, 1, 2 . \quad (12)$$

When $\alpha = \beta = 0$, the above equations reduce to the condition used by Bloch [43] to define the wave operator of his degenerate perturbation theory. Using Eqs. (5) and (11) one can easily show that the conditions of Eq. (12) can be rewritten as

$$\langle \phi_{\alpha k}^{(0)} | \phi_{\beta l} \rangle = \langle \phi_{\alpha k}^{(0)} | \phi_{\beta l}^{(0)} \rangle \quad \text{for all } \alpha, k, \beta, l . \quad (13)$$

The function $\phi_{\alpha k}$ defined by Eq. (12) or (13) has the property that the functional $J[\tilde{\tau}] = \langle \tilde{\tau} - \phi_{\alpha k} | \tilde{\tau} - \phi_{\alpha k} \rangle$, $\tilde{\tau} \in \mathcal{M}_0$, reaches its minimum when $\tilde{\tau} = \phi_{\alpha k}^{(0)}$ [34, 42]. Projecting Eq. (7) by $\phi_{\gamma m}^{(0)}$, using the localization conditions of Eq. (13), and the partitioning of the Hamiltonian $H = H_\gamma + V_\gamma$, we get a set of linear equations that can be used to express the coefficients $Q_{\alpha k}^{\beta l}$ in terms of the primitive functions $\phi_{\alpha k}$

$$\begin{aligned} \langle \phi_{\gamma m}^{(0)} | V_\gamma \phi_{\alpha k} \rangle + (E_m^{(0)} - E_k^{(0)}) \langle \phi_{\gamma m}^{(0)} | \phi_{\alpha k}^{(0)} \rangle \\ = \sum_\beta \sum_l Q_{\alpha k}^{\beta l} \langle \phi_{\gamma m}^{(0)} | \phi_{\beta l}^{(0)} \rangle . \end{aligned} \quad (14)$$

2.2 HS localization condition

HS localization is determined by the equation

$$P_\alpha [H_\beta, U] P_\beta = 0, \quad \text{for } \alpha \neq \beta, \quad \alpha, \beta = 0, 1, 2 , \quad (15)$$

and by the intermediate normalization condition

$$P_\alpha U P_\alpha = P_\alpha, \quad \text{for } \alpha = 0, 1, 2 . \quad (16)$$

Note that the intermediate normalization of the Bloch wave operator is implied by Eq. (12). The conditions represented by Eqs. (15) and (16) are equivalent to the following set of equations [46]

$$\langle \phi_{\alpha m}^{(0)} | H_\beta - E_l^{(0)} | \phi_{\beta l} \rangle = 0 \quad \text{for all } k, l, \text{ and } \alpha \neq \beta \quad (17)$$

and

$$\langle \phi_{\alpha k}^{(0)} | \phi_{\alpha l} \rangle = \delta_{kl} \quad \text{for all } \alpha . \quad (18)$$

Equations (17) and (18) were applied for the first time by Hirschfelder and Silbey [44] in the special case when the \mathbf{Q} matrix can be diagonalized by symmetry. From

Eqs. (7), (17), and (18) we get the following set of linear equations for $Q_{\alpha k}^{\beta l}$,

$$\langle \phi_{\gamma m}^{(0)} | V_{\alpha} \phi_{\alpha k} \rangle = \sum_{\beta} \sum_l Q_{\alpha k}^{\beta l} \langle \phi_{\gamma m}^{(0)} | \phi_{\beta l} \rangle . \quad (19)$$

HS localization does not seem to be related to any variational principle. It is very convenient in practice since it is preserved by the iteration process used to solve Eq. (7), see Appendix.

2.3 Kato localization condition

The most natural way to define the primitive wave function $\phi_{\alpha k}$ is to require that it is closer to $\phi_{\alpha k}^{(0)}$ than any other element of the target space \mathcal{M} . This means that $\phi_{\alpha k}$ is a projection of $\phi_{\alpha k}^{(0)}$ on the target space. This condition was used by Kato [45] in his formulation of degenerate perturbation theory. Since in developing perturbation equations the intermediate normalization, Eq. (18), is particularly convenient, we shall minimize the distance in the Hilbert space between $\phi_{\alpha k}$ and $\phi_{\alpha k}^{(0)}$ under the constraint that $\phi_{\alpha k}$ satisfies the intermediate normalization exactly. This can be done by minimizing the functional

$$G_{\alpha k}[\tilde{\tau}] = \langle \tilde{\tau} - \phi_{\alpha k}^{(0)} | \tilde{\tau} - \phi_{\alpha k}^{(0)} \rangle - \sum_l L_{\alpha k, l} (\langle \tilde{\tau} | \phi_{\alpha l}^{(0)} \rangle - \delta_{kl}) , \quad (20)$$

where $\tilde{\tau} \in \mathcal{M}$ is a trial function and $L_{\alpha k, l}$ are Lagrange multipliers. After some simple algebra we get the following set of necessary conditions for the primitive wave function $\phi_{\alpha k}$,

$$\langle \delta\tau | \phi_{\alpha k} - \sum_l \varepsilon_{\alpha k}^l \langle \delta\tau | \phi_{\alpha l}^{(0)} \rangle = 0 , \quad (21)$$

where $\delta\tau$ is an arbitrary function (variation) from the space \mathcal{M} , and the coefficients $\varepsilon_{\alpha k}^l = \delta_{kl} + L_{\alpha k, l}/2$ can be expressed in terms of the functions $\phi_{\alpha k}$

$$\varepsilon_{\alpha k}^l = \langle \phi_{\alpha l} | \phi_{\alpha k} \rangle . \quad (22)$$

By substituting Eq. (22) into Eq. (21) and replacing $\delta\tau$ by $\phi_{\beta l}$ we get the generalized Kato localization conditions

$$\langle \phi_{\beta l} | \phi_{\alpha k} \rangle - \sum_m \langle \phi_{\alpha m} | \phi_{\alpha k} \rangle \langle \phi_{\beta l} | \phi_{\alpha m}^{(0)} \rangle = 0 . \quad (23)$$

A similar expression for the nondegenerate case has been derived in Ref. [42]. The corresponding $Q_{\alpha k}^{\beta l}$ coefficients are solutions of the following system of linear equations

$$\begin{aligned} & \langle \phi_{\gamma m}^{(0)} | V_{\gamma} \phi_{\alpha k} \rangle + (E_m^{(0)} - E_k^{(0)}) \langle \phi_{\gamma m}^{(0)} | \phi_{\alpha k} \rangle \\ & = \sum_{\beta} \sum_l Q_{\alpha k}^{\beta l} \langle \phi_{\gamma m}^{(0)} | \phi_{\beta l} \rangle . \end{aligned} \quad (24)$$

2.4 Outline of the iterative procedure

Equation (7) can be solved iteratively using $\phi_{\alpha k}^{(0)}$ to start up the iterations. Consecutive approximations to the primitive wave functions are obtained from the equation

$$\phi_{\alpha k} = \phi_{\alpha k}^{(0)} + \hat{R}_{\alpha k} (-V_{\alpha} \phi_{\alpha k} + \sum_{\beta} \sum_l Q_{\alpha k}^{\beta l} \phi_{\beta l}) , \quad (25)$$

assuming that the matrix $Q_{\alpha k}^{\beta l}$ and all the primitive functions $\phi_{\alpha k}$ on the right-hand side of Eq. (25) are known from the previous iteration. The symbol $\hat{R}_{\alpha k}$ stands for the reduced resolvent $\hat{R}_{\alpha k} = (1 - P_{\alpha}) (H_{\alpha} - E_k^{(0)} + iP_{\alpha})^{-1}$. Equation (25) can be easily derived from Eq. (7) by partitioning the Hamiltonian H as $H_{\alpha} + V_{\alpha}$, moving V_{α} to the right-hand side, acting on both sides of the resulting equation with $\hat{R}_{\alpha k}$, and employing the identity $\hat{R}_{\alpha k} (H_{\alpha} - E_k^{(0)}) = 1 - P_{\alpha}$ together with the intermediate normalization of $\phi_{\alpha k}$, $P_{\alpha} \phi_{\alpha k} = \phi_{\alpha k}^{(0)}$.

Equation (25) can also be solved using an order-by-order perturbation expansion. Such an expansion is obtained when all V_{α} operators are multiplied by the same formal expansion parameter λ and the primitive functions are expanded in powers of this parameter. The iterative process of solving Eq. (25) is simpler computationally and is expected to show the same convergence pattern as the corresponding perturbation expansion, in the sense that the energy of the n th iteration and the sum of the perturbation corrections through the n th order will differ by terms of the order higher than n [15]. The functions $\phi_{\alpha k}$ for various α differ only by the permutation of the electronic coordinates, $\phi_{1k} = P_{13} \phi_{0k}$, $\phi_{2k} = P_{23} \phi_{0k}$, so it is sufficient to solve Eq. (25) for $\alpha = 0$. The coefficients $Q_{\alpha k}^{\beta l}$ can be obtained by solving the system of linear equations, characteristic to the applied localization scheme, i.e., Eqs. (14), (19), and (24).

We can now define the iterative processes corresponding to the three localization schemes introduced in Sects. 2.1–2.3. In the n th iteration we perform the following operations:

1. Assuming that the functions $\phi_{\alpha k}^{(n-1)}$ from the $(n-1)$ th iteration are known, the matrix $Q_{\alpha k}^{\beta l}(n)$ is calculated from the M independent sets of M linear equations in M unknowns

$$\begin{aligned} & \langle \phi_{\gamma m}^{(0)} | V_{\gamma} \phi_{\alpha k}^{(n-1)} \rangle + (E_m^{(0)} - E_k^{(0)}) \langle \phi_{\gamma m}^{(0)} | \phi_{\alpha k}^{(n-1)} \rangle \\ & = \sum_{\beta} \sum_l Q_{\alpha k}^{\beta l}(n) \langle \phi_{\gamma m}^{(0)} | \phi_{\beta l}^{(n-1)} \rangle . \end{aligned} \quad (26)$$

Equation (26) corresponds to the Kato localization, but similar equations for the Bloch and HS localizations can be easily derived from Eqs. (14) and (19), respectively.

2. The interaction energies of the n th iteration are obtained by diagonalizing the $Q_{\alpha k}^{\beta l}(n)$ matrix. If the zeroth-order functions are not completely degenerate, the matrix $\tilde{Q}_{\alpha k}^{\beta l}$ of Eq. (8) is diagonalized and the zeroth-order energies $E_k^{(0)}$ are subtracted from appropriate eigenvalues.

3. The wave functions $\phi_{\alpha k}^{(n-1)}$ and the matrix $Q_{\alpha k}^{\beta l}(n)$ are used to determine new approximation $\bar{\phi}_{\alpha k}^{(n)}$ to the wave functions $\phi_{\alpha k}$:

$$\bar{\phi}_{0k}^{(n)} = \phi_{0k}^{(0)} + \hat{R}_{0k} \left(-V_0 \phi_{0k}^{(n-1)} + \sum_{\beta} \sum_l Q_{0k}^{\beta l}(n) \phi_{\beta l}^{(n-1)} \right) , \quad (27)$$

$$\bar{\phi}_{1k}^{(n)} = P_{13} \bar{\phi}_{0k}^{(n)} , \text{ and } \bar{\phi}_{2k}^{(n)} = P_{23} \phi_{0k}^{(n)} .$$

4. In general, the iterative procedure, Eqs. (26) and (27), does not automatically preserve the localization of the wave function, i.e., the functions $\bar{\phi}_{\alpha k}^{(n)}$ do not fulfill the localization conditions. Therefore, a linear transformation (the so-called relocalization)

$$\phi_{\alpha k}^{(n)} = \sum_{\beta} \sum_l c_{\alpha k}^{\beta l}(n) \bar{\phi}_{\beta l}^{(n)}, \quad (28)$$

is necessary to assure a proper localization of the wave function in each iteration. The relocalization coefficients $c_{\alpha k}^{\beta l}(n)$ are obtained by imposing the localization conditions on the wave function $\phi_{\alpha k}^{(n)}$. For the Bloch scheme this is done by solving the set of linear equations resulting from Eq. (13),

$$\sum_{\gamma} \sum_m c_{\beta l}^{\gamma m}(n) \langle \phi_{\alpha k}^{(0)} | \bar{\phi}_{\gamma m}^{(n)} \rangle = \langle \phi_{\alpha k}^{(0)} | \phi_{\beta l}^{(0)} \rangle, \quad (29)$$

for $\alpha, \beta = 0, 1, 2$ and $k, l = 1, \dots, D$. In HS theory the functions $\bar{\phi}_{\alpha k}^{(n)}$ automatically fulfil the localization conditions, Eqs. (17) and (18), so there is no need for the relocalization (see Appendix). The Kato localization of the wave function is not preserved during the iterative process, Eq. (27), and relocalization is necessary. Substituting Eq. (28) into Eq. (23) gives a system of cubic equations for the relocalization coefficients $c_{\alpha k}^{\beta l}(n)$. These equations can be rigorously linearized by noting that in the n th iteration the projection against $\phi_{\beta l}^{(n)}$ in Eq. (23) can be replaced by projection against $\bar{\phi}_{\beta l}^{(n)}$. The resulting system of linear equations

$$\sum_{\gamma} \sum_m c_{\alpha k}^{\gamma m}(n) \langle \bar{\phi}_{\beta l}^{(n)} | \bar{\phi}_{\gamma m}^{(n)} \rangle - \sum_m \bar{e}_{\alpha k}^m(n) \langle \bar{\phi}_{\beta l}^{(n)} | \phi_{\alpha m}^{(0)} \rangle = 0 \quad (30)$$

is sufficient to determine the coefficients $c_{\alpha k}^{\gamma m}(n)$ and the parameters $\bar{e}_{\alpha k}^m(n) = \langle \bar{\phi}_{\alpha m}^{(n)} | \bar{\phi}_{\alpha k}^{(n)} \rangle$ if it is supplemented by the equation

$$\sum_{\gamma} \sum_m c_{\alpha k}^{\gamma m}(n) \langle \bar{\phi}_{\gamma m}^{(n)} | \phi_{\alpha l}^{(0)} \rangle = \delta_{kl} \quad (31)$$

resulting from the intermediate normalization condition, Eq. (18).

In comparison to the order-by-order perturbation expansion of the effective interaction matrix the iterative process described above has the advantage that only the results of the last iteration need to be stored.

3 Application to Rydberg states of helium hydride

3.1 Computational details

For the helium atom we used a $[5s3pld]$ basis set. The isotropic part of this basis was represented by the (61111) contraction of the 10s set of van Duijneveldt [47]. The polarization part was taken from the basis of Gutowski et al. [48] optimized for the dispersion energy of He_2 (the exponents of the 3p set were rounded to four digits).

The hydrogenic orbitals with $n \leq 3$ were represented by large contracts of even-tempered Gaussian functions. The a and b parameters of these functions (the k th ex-

Table 1. Parameters of the contracted part of the basis set for the hydrogen atom

Orbital	a	b	k_{\max}	Contraction
1s	0.025	1.67	40	(10,10,10,10)
2s	0.00072	1.36	40	(10,10,10,10)
3s	0.00215	1.55	10	(10)
2p	0.005	1.57	30	(15,15)
3p	0.00216	1.55	15	(15)
3d	0.00285	1.69	15	(15)

ponent is equal to ab^{k-1}) were optimized for the energy of the n th state of the hydrogen atom ($n \leq 3$). In the resulting $[9s3p1d]$ basis set (see Table 1 for a more detailed specification) the energies of the 1s, 2s, and 2p states were reproduced with errors smaller than 10^{-12} hartree. The errors in the energies of the $n = 3$ states were smaller than 10^{-10} hartree. This basis was extended to the $[10s4p2d]$ set by adding diffuse functions with exponents 0.04282 (s function), 0.0179 (p function), and 0.0362 (d function) optimized for the static dipole polarizabilities of the 2s and 2p states of the hydrogen atom. The energy of the helium atom in the dimer basis set obtained is equal to -2.898861188 a.u. for $R = 3$ bohr and -2.898852105 a.u. for $R = 7$ bohr.

The three-electron configuration space used in FCI and perturbation theory calculations is spanned by the basis

$$\Psi_{\kappa\lambda\mu}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \frac{1}{\sqrt{2(1 + \delta_{\kappa\lambda})}} [\kappa(\mathbf{r}_1)\lambda(\mathbf{r}_2) + \kappa(\mathbf{r}_2)\lambda(\mathbf{r}_1)]\mu(\mathbf{r}_3), \quad (32)$$

where κ, λ denote the self-consistent field (SCF) orbitals of the helium atom, and μ is an orbital of the hydrogen atom. We can work with the space of functions which are symmetric in \mathbf{r}_1 and \mathbf{r}_2 since we compute only the function ϕ_{0k} and the symmetric component of the doublet transforming according to $[2, 1]$ irrep. The orbitals κ, λ , and μ were computed in the full basis of the dimer. Since $C_{\infty v}$ is a symmetry group of both H and H_0 , we could consider the states of HeH that belong to different representations of $C_{\infty v}$ separately. This means that Eqs. (9) and (25) were solved separately for the model spaces transforming according to Σ, Π and Δ representations of $C_{\infty v}$. The plots of the potential energy curves for the states considered by us are given, for example, in Ref. [37].

The ATMOL [49] suite of codes was used to compute the atomic integrals and the SCF vectors of the He atom. The four-index transformation to the molecular basis was taken from the SAPT suite of codes [50]. The FCI energies were computed with the use of the code of Duch [51] based on the Davidson algorithm [52]. The interaction energies computed from the FCI energies using the supermolecular approach and corrected for basis set superposition error (BSSE) using the conventional counterpoise correction [53] will be referred as the FCI interaction energies.

As discussed in the Introduction the excited states of HeH are of considerable theoretical interest [37, 38]. However, in most papers [38] only the total energies of

various states of the HeH molecule were reported, so it is difficult to estimate the accuracy of the FCI interaction energies computed in the present paper. To our knowledge, only van Hemert and Peyerimhoff [37] have reported the interaction energies for the lowest ten states of HeH. Unfortunately, the results presented in Ref. [37] were not corrected for BSSE. For the smaller interatomic distance considered by us ($R = 3$ bohr) BSSE represents a small fraction of the interaction energy, so a comparison of our FCI results with the results of Ref. [37] is possible. It turns out that for all states considered in the present paper the results of Ref. [37] agree with our values to within a few percent. To compare the results at $R = 7$ bohr one should estimate the BSSE. One can notice that the interaction energies for $R = 20$ bohr reported in Ref. [37] are very large, while they should be close to zero (with an accuracy of a few micro hartree). Assuming that the results at $R = 20$ represent pure BSSE or size-consistency error, and that these errors show a weak dependence on R , one can approximately correct the results of Ref. [37] at $R = 7$ bohr by subtracting from their interaction ener-

gies at $R = 7$ bohr the values for $R = 20$ bohr. The results of Ref. [37] corrected in this way agree with our results to within a few percent for the $A^2\Sigma^+$, $C^2\Sigma^+$, and $B^2\Pi$ states.

3.2 Numerical results and discussion

The convergence of the iterative procedure described in Sect. 2.4 for the three localization schemes introduced in Sects. 2.1–2.3 has been tested by performing numerical calculations for the lowest excited states of the $\text{He} \cdots \text{H}$ system. We present the results for two interatomic separations, $R = 3$ and $R = 7$ bohr. The smaller distance corresponds to the repulsive region of the $X^2\Sigma^+$ and $C^2\Sigma^+$ states and to the region of the chemical minimum for the $A^2\Sigma^+$ and $B^2\Pi$ states. The larger distance corresponds approximately to the van der Waals minimum of the ground state.

We first consider the active sets consisting of the $2s$ and $2p_z$ orbitals for the Σ symmetry, and of the $2p_x$ orbital for the Π symmetry. In Tables 2 and 3 we present

Table 2. Convergence of interaction energies for the $A^2\Sigma^+$, $C^2\Sigma^+$, and $B^2\Pi$ states of HeH at $R = 3$ bohr in terms of the percentage errors relative to the FCI interaction energy. The active set consists of the $2s$ and $2p_z$ orbitals for the Σ states and of the $2p_x$ orbital for

the Π state. The FCI interaction energies for the $A^2\Sigma^+$, $C^2\Sigma^+$, and $B^2\Pi$ states are -13.689 , 16.398 , and -15.652 millihartree, respectively

n	$A^2\Sigma^+$			$C^2\Sigma^+$			$B^2\Pi$		
	Bloch	HS	Kato	Bloch	HS	Kato	Bloch	HS	Kato
1	-94.599	-94.599	-94.599	271.186	271.186	271.186	-88.073	-88.073	-88.073
2	-34.399	-34.399	-34.399	172.841	172.841	172.841	-32.150	-32.150	-32.150
3	-21.942	-21.935	-21.939	156.279	155.910	153.019	-20.944	-20.927	-20.948
4	-13.303	-13.312	-13.327	103.412	106.233	99.667	-13.490	-13.485	-13.494
5	-8.159	-8.102	-8.241	90.181	88.278	86.969	-9.245	-9.245	-9.247
6	-3.814	-3.771	-4.107	42.559	44.374	44.060	-6.362	-6.367	-6.362
7	-1.345	-1.039	1.890	44.807	36.702	50.898	-4.482	-4.489	-4.481
8	2.307	2.566	0.831	-11.370	-11.601	7.034	-3.199	-3.207	-3.197
9	2.333	3.346	0.934	30.509	8.250	49.992	-2.330	-2.339	-2.328
10	9.600	10.216	3.888	-71.678	-70.784	-23.245	-1.731	-1.740	-1.728
20	2810.694	2455.767	17.777	-189.955	-193.408	-92.865	-0.311	-0.315	-0.309

Table 3. Convergence of the interaction energies for the $A^2\Sigma^+$, $C^2\Sigma^+$, and $B^2\Pi$ states of HeH at $R = 7$ bohr in terms of the percentage errors relative to the FCI interaction energy. The active set consists of the $2s$ and $2p_z$ orbitals for the Σ states and of the $2p_x$

orbital for the Π state. The FCI interaction energies for the $A^2\Sigma^+$, $C^2\Sigma^+$, and $B^2\Pi$ states are -0.13885 , 6.8185 , and -0.25558 millihartree, respectively

n	$A^2\Sigma^+$			$C^2\Sigma^+$			$B^2\Pi$		
	Bloch	HS	Kato	Bloch	HS	Kato	Bloch	HS	Kato
1	-96.427	-96.427	-96.427	83.183	83.183	83.183	-73.775	-73.775	-73.775
2	-2.099	-2.099	-2.099	77.082	77.082	77.082	-4.501	-4.501	-4.501
3	-0.596	-0.596	-0.596	95.866	97.279	94.636	-2.404	-2.404	-2.404
4	-0.292	-0.291	-0.290	98.164	101.615	93.328	-1.113	-1.113	-1.113
5	-0.224	-0.223	-0.221	102.662	107.409	93.883	-0.815	-0.815	-0.815
6	-0.188	-0.187	-0.183	103.238	109.426	89.849	-0.632	-0.632	-0.632
7	-0.167	-0.167	-0.160	103.165	110.359	85.807	-0.532	-0.532	-0.532
8	-0.152	-0.152	-0.144	101.433	109.495	80.499	-0.460	-0.460	-0.460
9	-0.141	-0.142	-0.131	98.927	107.551	75.215	-0.404	-0.404	-0.404
10	-0.133	-0.134	-0.121	95.572	104.573	69.746	-0.359	-0.359	-0.359
20	-0.088	-0.090	-0.068	52.968	59.648	30.599	-0.149	-0.149	-0.149
30	-0.056	-0.057	-0.040	25.726	29.255	13.863	-0.086	-0.086	-0.086
40	-0.017	-0.016	-0.014	13.610	15.741	6.894	-0.058	-0.058	-0.058

the convergence of the interaction energies for the $A^2\Sigma^+$, $C^2\Sigma^+$, and $B^2\Pi$ states computed using Bloch, HS, and Kato localizations. Inspection of Table 2 shows that at $R = 3$ bohr convergence is found only for the $B^2\Pi$ state. For the Σ states we see a slow apparent convergence for low orders, and the onset of rapid divergence for high orders. The observed convergence properties do not significantly depend on the localization conditions employed in the calculations. For $R = 7$ bohr the iterative procedure appears to converge for all three states, although for the C state this convergence is pathologically slow (see Table 3). Again the results are almost independent of the localization employed, although the Kato procedure appears to give slightly better results than other localizations. We also computed the Padé approximants for the divergent and slowly convergent series but we found no significant improvement in convergence properties.

Closer inspection of the computed interaction energies revealed that the divergence seen for $R = 3$ is only apparent. Very high order calculations with a smaller basis set showed that the sequence of energies that should approximate the energy of the A state actually converges to the energy of the $X^2\Sigma^+$ ground state, while the sequence designed to approximate the energy of the C state converges to the energy of the A state. This unusual behavior is related to the fact that orthogonality of the wave functions for the A and C states to the wave function of the X state was not imposed during the iterative procedure. As a result the interaction energies converge to the ground-state energy despite the fact that the excited-state eigenfunctions of H_0 were used as the zeroth-order wave functions (this problem does not occur for the $B^2\Pi$ state because this state is orthogonal by symmetry to the X ground state).

To overcome the problem described above we considered a larger model space with the $1s$ hydrogen orbital included in the active space. Test calculations showed that also in this case the HS and Kato methods are not clearly superior to the Bloch method (which is the simplest method based on some kind of minimum-distance

principle) so all results reported were obtained with the use of Bloch localization. The interaction energies for the A state obtained when the ground state is included in the model space (i.e., with the $1s$, $2s$, and $2p_z$ orbitals in the active set) are presented in Table 4. From Table 4 it can be seen that inclusion of the X state in the model space prevents the high-order ‘‘collapse’’ to the X state, and the iterative procedure is convergent. In the region of the chemical minimum, $R = 3$ bohr, the tenth-order treatment reproduces the FCI energy with an error of 2%. At this distance convergence is not particularly fast, but this is not surprising, since the wave function for the A state in this region differs substantially from its asymptotic form. At $R = 7$ bohr convergence is much faster. The second iteration reproduces 98% of the FCI result, and the error of the third iteration is only 0.6%. Afterwards, the convergence slows down, but nonetheless the 30th iteration reproduces the interaction energy with an error of -0.06% . We also found that the fast convergence of the symmetry-adapted perturbation series for the X state was not improved by this extension of the model space.

The situation is very different for the C state. The inclusion of the X state in the model space does not improve the convergence for this state, and the convergence pattern is qualitatively the same as presented in Tables 2 and 3. This very unsatisfactory convergence can be due to a strong coupling of the C state with the higher Σ states of HeH. Indeed, it has been reported [36] that the $C^2\Sigma^+$ state can interact with higher-lying Σ states, especially with the $D^2\Sigma^+$ state. In order to check if convergence for the C state improves by including in the model space the D state and two other states that are asymptotically degenerate with it we performed calculations with the model space containing the six lowest Σ states, i.e., with the $3s$, $3p_z$, and $3d_{zz}$ orbitals added to the active set. The results, presented in Table 5, show that the use of a larger model space improves the convergence significantly, although the observed convergence rate is still rather slow, and shows an oscillatory behavior. This

Table 4. Convergence of the interaction energy for the $A^2\Sigma^+$ state of HeH. The X, A, and $C^2\Sigma^+$ states are included in the model space. Bloch localization is assumed. $E(n)$ denotes the interaction energy of the n th iteration, $\varepsilon^{(n)} = E(n) - E(n-1)$ ($\varepsilon^{(1)} = E(1)$), and

$\delta(n) = 100(E(n) - E_{\text{int}})/E_{\text{int}}$ is the percentage error with respect to the FCI interaction energy E_{int} . Energies are in hartree. The symbol $(-N)$ denotes 10^{-N} .

n	$R = 3$ bohr			$R = 7$ bohr		
	$\varepsilon^{(n)}$	$E(n)$	$\delta(n)$	$\varepsilon^{(n)}$	$E(n)$	$\delta(n)$
1	-0.71497(-3)	-0.71497(-3)	-94.777	-0.49613(-5)	-0.49613(-5)	-96.427
2	-0.82032(-2)	-0.89182(-2)	-34.851	-0.13097(-3)	-0.13593(-3)	-2.099
3	-0.16246(-2)	-0.10543(-1)	-22.983	-0.20862(-5)	-0.13802(-3)	-0.597
4	-0.11114(-2)	-0.11654(-1)	-14.864	-0.42358(-6)	-0.13844(-3)	-0.292
5	-0.61204(-3)	-0.12266(-1)	-10.393	-0.93847(-7)	-0.13854(-3)	-0.224
6	-0.46656(-3)	-0.12733(-1)	-6.985	-0.50156(-7)	-0.13859(-3)	-0.188
7	-0.24996(-3)	-0.12983(-1)	-5.159	-0.29303(-7)	-0.13862(-3)	-0.167
8	-0.23881(-3)	-0.13222(-1)	-3.414	-0.20434(-7)	-0.13864(-3)	-0.152
9	-0.80384(-4)	-0.13302(-1)	-2.827	-0.15009(-7)	-0.13865(-3)	-0.141
10	-0.15965(-3)	-0.13462(-1)	-1.661	-0.11692(-7)	-0.13867(-3)	-0.133
20	-0.38621(-3)	-0.13835(-1)	1.069	-0.45797(-8)	-0.13873(-3)	-0.089
30	-0.50842(-6)	-0.13634(-1)	-0.401	-0.33774(-8)	-0.13877(-3)	-0.061
FCI		-0.13689(-1)			-0.13885(-3)	

Table 5. Convergence of the interaction energies for the $C^2\Sigma^+$ state of HeH. The lowest six states of $^2\Sigma^+$ symmetry are included in the model space. Bloch localization is assumed. Energies are in hartree. See the caption to Table 4 for an explanation of the symbols

n	$R = 3$ bohr			$R = 7$ bohr		
	$\varepsilon^{(n)}$	$E(n)$	$\delta(n)$	$\varepsilon^{(n)}$	$E(n)$	$\delta(n)$
1	0.42908(-1)	0.42908(-1)	161.670	0.10552(-1)	0.10552(-1)	54.760
2	-0.12021(-1)	0.30886(-1)	88.358	-0.98229(-3)	0.95700(-2)	40.354
3	-0.24428(-2)	0.28444(-1)	73.461	0.25616(-3)	0.98262(-2)	44.111
4	-0.18109(-2)	0.26633(-1)	62.417	-0.30429(-3)	0.95219(-2)	39.648
5	-0.26086(-2)	0.24024(-1)	46.509	-0.16914(-3)	0.93528(-2)	37.168
6	0.54659(-3)	0.24571(-1)	49.843	-0.26153(-3)	0.90912(-2)	33.332
7	-0.35029(-2)	0.21068(-1)	28.480	-0.22624(-3)	0.88650(-2)	30.014
8	0.31930(-2)	0.24261(-1)	47.953	-0.24409(-3)	0.86209(-2)	26.434
9	-0.56021(-2)	0.18659(-1)	13.789	-0.21884(-3)	0.84021(-2)	23.225
10	0.97119(-2)	0.28371(-1)	73.016	-0.21659(-3)	0.81855(-2)	20.048
20	-0.14375(-2)	0.23096(-1)	40.851	-0.74746(-4)	0.68963(-2)	1.141
30	-0.40691(-3)	0.19673(-1)	19.972	-0.36523(-4)	0.65526(-2)	-3.900
40	-0.10527(-3)	0.16986(-1)	3.585	-0.44310(-3)	0.62927(-2)	-7.712
FCI		0.16398(-1)			0.68185(-2)	

Table 6. Convergence of the interaction energies for the $3^2\Pi$ state of HeH. The B, E, and $3^2\Pi$ states are included in the model space. Bloch localization is assumed. Energies are in hartree. See the caption to Table 4 for an explanation of the symbols

n	$R = 3$ bohr			$R = 7$ bohr		
	$\varepsilon^{(n)}$	$E(n)$	$\delta(n)$	$\varepsilon^{(n)}$	$E(n)$	$\delta(n)$
1	0.41935(-3)	0.41935(-3)	-102.921	-0.25939(-5)	-0.25939(-5)	-98.935
2	-0.94821(-2)	-0.90628(-2)	-36.878	-0.23593(-3)	0.23853(-3)	-2.058
3	-0.18600(-2)	-0.10923(-1)	-23.924	-0.38395(-5)	-0.24236(-3)	-0.481
4	-0.12161(-2)	-0.12139(-1)	-15.453	-0.75126(-6)	-0.24312(-3)	-0.173
5	-0.73424(-3)	-0.12873(-1)	-10.339	-0.14719(-6)	-0.24326(-3)	-0.113
6	-0.49279(-3)	-0.13366(-1)	-6.907	-0.75150(-7)	-0.24334(-3)	-0.082
7	-0.32474(-3)	-0.13691(-1)	-4.645	-0.45865(-7)	-0.24338(-3)	-0.063
8	-0.21801(-3)	-0.13909(-1)	-3.127	-0.31974(-7)	-0.24342(-3)	-0.050
9	-0.14521(-3)	-0.14054(-1)	-2.115	-0.23124(-7)	-0.24344(-3)	-0.040
10	-0.97579(-4)	-0.14152(-1)	-1.436	-0.17142(-7)	-0.24346(-3)	-0.033
20	-0.20447(-5)	-0.14348(-1)	-0.066	-0.17496(-8)	-0.24351(-3)	-0.011
30	-0.16430(-6)	-0.14354(-1)	-0.028	-0.57363(-9)	-0.24352(-3)	-0.007
40	-0.81604(-7)	-0.14355(-1)	-0.021	-0.33304(-9)	-0.24352(-3)	-0.006
FCI		-0.14358(-1)			-0.24354(-3)	

rather disappointing result suggests that despite the use of an extended model space, the wave function for the C state is very strongly perturbed by interactions with higher states.

Since convergence for $C^2\Sigma^+$ is not satisfactory, it is interesting to check if the relatively poor performance of the perturbation method is due to coupling with higher states, or if our method has, in general, convergence problems for the highest state from the asymptotically degenerate set. In Table 6 we report the interaction energies for the $3^2\Pi$ state (this is the higher state of the asymptotically degenerate pair of Π states). The active set employed consists of the $2p_x$, $3p_x$, and $3d_{xz}$ orbitals, i.e., the model space includes the B, E, and $3^2\Pi$ states. The convergence pattern observed is very similar to that found for the A state, cf. Table 4. In particular, the results for $R = 7$ bohr are very encouraging: the second iteration reproduces almost 98% of the interaction energy. Similarly good convergence was also found for the two other states included in the model space, i.e. for the $B^2\Pi$ and $E^2\Pi$ states. This suggests that the unsatisfactory convergence for the C state is an exception

due to strong interactions of this state with higher Σ states.

In Table 7 we report results for the lowest state of Δ symmetry. In this case the active set consists of the $3d_{xy}$ orbital. Very good convergence is observed for this state, especially for the larger distance.

4 Conclusions

In this paper we have developed a new method for the calculation of the interaction energies for open-shell complexes, based on symmetry-adapted perturbation theory. The new formalism can be viewed as an extension of the theory of model spaces and wave operators to the case of perturbation theories with symmetry adaptation. We have tested the proposed approach on the model system consisting of a ground state helium atom interacting with an excited hydrogen atom. Using several excited Σ , Π , and Δ states of HeH as examples we have shown that by properly choosing the zeroth-order model space one can obtain accurate

Table 7. Convergence of the interaction energies for the $1^2\Delta$ state of HeH. The first Δ state is included in the model space. Bloch localization is assumed. Energies are in hartree. See the caption to Table 4 for an explanation of the symbols

n	$R = 3$ bohr			$R = 7$ bohr		
	$\varepsilon^{(n)}$	$E(n)$	$\delta(n)$	$\varepsilon^{(n)}$	$E(n)$	$\delta(n)$
1	0.44512(-3)	0.44512(-3)	-103.222	-0.32481(-5)	-0.32481(-5)	-98.571
2	-0.90953(-2)	-0.86502(-2)	-37.387	-0.21991(-3)	-0.22315(-3)	-1.840
3	-0.18373(-2)	-0.10487(-1)	-24.088	-0.32902(-5)	-0.22644(-3)	-0.393
4	-0.11837(-2)	-0.11671(-1)	-15.520	-0.60325(-6)	-0.22705(-3)	-0.128
5	-0.72131(-3)	-0.12392(-1)	-10.299	-0.11144(-6)	-0.22716(-3)	-0.079
6	-0.47992(-3)	-0.12872(-1)	-6.825	-0.57208(-7)	-0.22722(-3)	-0.054
7	-0.31631(-3)	-0.13189(-1)	-4.535	-0.35829(-7)	-0.22725(-3)	-0.038
8	-0.21044(-3)	-0.13399(-1)	-3.012	-0.24770(-7)	-0.22728(-3)	-0.027
9	-0.13962(-3)	-0.13539(-1)	-2.001	-0.17534(-7)	-0.22729(-3)	-0.019
10	-0.92839(-4)	-0.13632(-1)	-1.329	-0.12531(-7)	-0.22731(-3)	-0.014
20	-0.15568(-5)	-0.13812(-1)	-0.021	-0.47534(-9)	-0.22734(-3)	0.000
30	-0.23576(-7)	-0.13815(-1)	0.000	-0.93885(-11)	-0.22734(-3)	0.000
FCI		-0.13815(-1)			-0.22734(-3)	

interaction energies near the van der Waals minimum of the ground state provided that the state under considerations is not strongly perturbed by higher-lying excited states.

It is worth noting that the iterative procedure based on Bloch, HS, and Kato localization conditions is compatible, in the asymptotic region, with the degenerate polarization (Rayleigh-Schrödinger) perturbation expansion. This means that the computed interaction energies can be interpreted in terms of the electrostatic, resonance, induction, and dispersion contributions, and that they have well-defined asymptotic large- R behavior governed by multipole expansion [54]. The multireference structure of our approach also enables the method to be extended to many-electron systems using the techniques of multireference coupled-cluster theory [55]. Work in this direction is in progress in our group.

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Appendix

In this Appendix we shall prove that the HS wave functions, defined recursively as

$$\bar{\phi}_{\alpha k}^{(n)} = \phi_{\alpha k}^{(0)} + \hat{R}_{\alpha k} [-V_{\alpha} \phi_{\alpha k}^{(n-1)} + \sum_{\beta} \sum_l Q_{\alpha k}^{\beta l}(n) \phi_{\beta l}^{(n-1)}], \quad (\text{A1})$$

fulfill the localization conditions of Eqs. (17) and (18) if this condition is fulfilled by the functions of the $(n-1)$ th iteration.

To prove this we act on both sides of Eq. (A1) with the operator $(H_{\alpha} - E_k^{(0)})$, and project the resulting equation on $\phi_{\gamma m}^{(0)}$. This gives

$$\begin{aligned} \langle \phi_{\gamma m}^{(0)} | (H_{\alpha} - E_k^{(0)}) \bar{\phi}_{\alpha k}^{(n)} \rangle &= \langle \phi_{\gamma m}^{(0)} | V_{\alpha} \phi_{\alpha k}^{(n-1)} \rangle \\ &\quad - \sum_{\beta} \sum_l Q_{\alpha k}^{\beta l}(n) \langle \phi_{\gamma m}^{(0)} | \phi_{\beta l}^{(n-1)} \rangle \\ &\quad - \langle \phi_{\gamma m}^{(0)} | P_{\alpha} V_{\alpha} \phi_{\alpha k}^{(n-1)} \rangle \\ &\quad + \sum_{\beta} \sum_l Q_{\alpha k}^{\beta l}(n) \langle \phi_{\gamma m}^{(0)} | P_{\alpha} \phi_{\beta l}^{(n-1)} \rangle. \end{aligned} \quad (\text{A2})$$

When deriving Eq. (A2) we used the identity $(H_{\alpha} - E_k^{(0)}) \hat{R}_{\alpha} = 1 - P_{\alpha}$. The sum of the first two terms on the right-hand side of Eq. (A2) is equal to zero because in HS theory the coefficients $Q_{\alpha k}^{\beta l}(n)$ fulfill the equation

$$\langle \phi_{\gamma m}^{(0)} | V_{\alpha} \phi_{\alpha k}^{(n-1)} \rangle = \sum_{\beta \gamma} \sum_l Q_{\alpha k}^{\beta l}(n) \langle \phi_{\gamma m}^{(0)} | \phi_{\beta l}^{(n-1)} \rangle. \quad (\text{A3})$$

Using the definition of P_{α} , Eq. (5), the sum of the third and fourth terms can be rewritten as

$$\begin{aligned} \sum_p \langle \phi_{\gamma m}^{(0)} | \phi_{\alpha p}^{(0)} \rangle \left[- \langle \phi_{\alpha p}^{(0)} | V_{\alpha} \phi_{\alpha k}^{(n-1)} \rangle \right. \\ \left. + Q_{\alpha k}^{\alpha p} + \sum_{\beta \neq \alpha} \sum_l Q_{\alpha k}^{\beta l}(n) \langle \phi_{\alpha p}^{(0)} | \phi_{\beta l}^{(n-1)} \rangle \right]. \end{aligned} \quad (\text{A4})$$

The expression in square brackets vanishes as a consequence of Eq. (A3). This proves that

$$\langle \phi_{\gamma m}^{(0)} | (H_{\alpha} - E_k^{(0)}) \bar{\phi}_{\alpha k}^{(n)} \rangle = 0. \quad (\text{A5})$$

The function $\bar{\phi}_{\alpha k}^{(n)}$ fulfills the intermediate normalization condition, Eq. (18), since $\hat{R}_{\alpha} \phi_{\alpha l}^{(0)} \equiv 0$ for $l = 1, \dots, D$.

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