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Direct calculation of interaction-induced molecular properties: An application to the relativistic mass-velocity and Darwin terms in the interaction energy of hydrogen atoms

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Interaction-induced properties, including the interaction energy itself, are difficult to compute using explicitly correlated basis functions since bases corresponding to noninteracting atoms are not defined in this case. We propose a direct method of calculation in which no subtraction of exact or approximate atomic properties is required. To test the method we computed the one-electron Darwin and mass-velocity contributions to the interaction energy of two ground-state hydrogen atoms at separations close to the van der Waals minimum in the triplet state. To verify the accuracy at larger distances, we also computed the constants determining the asymptotic long-range behavior of the investigated contributions. Our results, obtained with a Gaussian geminal basis, appear to be more accurate than the results of earlier variational calculations employing explicitly correlated exponential functions. When the same basis sets are employed, our method gives results very close to the so-called "monomer-contraction method" proposed recently by Cencek *et al.* [W. Cencek *et al.*, Phys. Rev. Lett. **95**, 23304 (2005)], which confirms the soundness of the latter approach. To extend the validity of our calculations to very large interatomic separations R, we provide damping functions accounting for the retardation effects and producing the correct $1/R^7$ long-range decrease of the computed relativistic corrections.

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I. INTRODUCTION

The interaction-induced property is defined as the change of certain property of the system caused by the effect of interatomic or intermolecular interactions. In this work we shall consider only first-order properties given, via the Hellmann-Feynman theorem, as the expectation value of appropriate operators. Specifically, the interaction-induced property ΔW corresponding to the operator W is defined as

$$\Delta W = \langle\psi|W|\psi\rangle - \langle\phi_A|W_A|\phi_A\rangle - \langle\phi_B|W_B|\phi_B\rangle, \tag{1}$$

where ϕ_A, ϕ_B, and ψ are the electronic wave functions for the noninteracting monomers A and B (atoms or molecules) and for the whole interacting system, respectively, while W_X, $X=A,B$, is the operator of the same form as W, but with summations over electrons and nuclei limited to particles belonging to monomer X. The definition (1) is based on the Born-Oppenheimer approximation; i.e., the nuclei of A and B are fixed at the same positions as in the whole interacting system AB. The quantity ΔW depends on the distance R between interacting monomers and possibly on their mutual spatial orientation.

ΔW can be computed directly from its definition; however, for weakly interacting atoms and molecules, the final result of the subtractions in Eq. (1) is usually several orders of magnitude smaller than the errors with which the subtracted expectation values are calculated. Thus, ΔW can be expected to be accurate only if a significant cancellation of these errors occurs. Such a cancellation indeed takes place provided that (i) the electronic structure method used to approximate ψ is size consistent [1–3] and (ii) "basis-set consistency" [4] in computing ψ, ϕ_A, and ϕ_B can be achieved and an appropriate basis-set superposition correction can be applied [5,6]. These two conditions are fulfilled for certain electronic structure methods based on the molecular orbital model (e.g., for the single-reference Møller-Plesset [1,2] or coupled-cluster theories [7]). They are not fulfilled, however, in a Rayleigh-Ritz-type variational calculation employing explicitly correlated basis functions. This approach can be viewed as by far the most accurate method to compute the electronic energy [8], but it fails to be size consistent. This is due to the fact that no unambiguous correspondence between explicitly correlated dimer and monomer bases can be established [9] which would enable even a numerical test of size consistency. In practice for a given variationally optimized function ψ it is impossible to find monomer bases which would make the right-hand side (rhs) of Eq. (1) vanish at large R. This problem appears not only in calculations of molecular properties [10], but also in variational calculations of the interaction energy [11]—i.e., when the W, W_A, and W_B operators in Eq. (1) are replaced by appropriate electronic Hamiltonians.

Two approaches to cope with this difficulty have been proposed. In the first, *brute force* (BF) approach, all terms in Eq. (1) are computed as accurately as possible, taking the exact values of the monomer terms if available. This approach works very well when ΔW is not too small. It must become inaccurate at large R, however, since ΔW does not vanish in the limit of infinite R. In practice, the last two monomer terms in Eq. (1) are always more accurate than the first term. When the interaction energy is calculated from this equation it becomes therefore too small [11] at large R and unphysically positive asymptotically.

Another, more sophisticated and significantly more accurate approach has been recently proposed by Cencek *et al.* [9]. The main idea of this approach, referred to as the *monomer contraction* (MC) method, is to extend the set of basis functions χ_k, $i=1,\ldots,M$, used to expand ψ, by a single function ψ_0 of the form

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$$\psi_0 = \Pi \phi_A \phi_B, \tag{2}$$

where ϕ_A and ϕ_B are carefully optimized monomer wave functions—fixed in further calculations—and Π is a symmetry projector assuring that ψ_0 has the same exchange and spin symmetry as ψ. The trial function in the Rayleigh-Ritz variational calculations for ψ is assumed in the form

$$\tilde{\psi} = c_0\psi_0 + \sum_{i=1}^{M} c_k\chi_k, \tag{3}$$

and once the linear parameters c_k are optimized, ΔW is computed from Eq. (1). This procedure is not free from the formal drawbacks of the BF method since the second term on the rhs in Eq. (3) gives a nonvanishing contribution to ΔW (and to the interaction energy) at infinite intermonomer separation. Nevertheless, Cencek *et al.* have shown [9] that for two helium atoms interacting at the equilibrium separation of $R=5.6$ bohrs the MC method gives very good results provided that the monomer functions ϕ_A and ϕ_B employed are of sufficiently good quality and the nonlinear parameters defining basis functions χ_k are optimized *in the presence* of the function ψ_0 (i.e., ψ_0 is not added to a basis optimized earlier without this function).

In the present communication we propose an alternative method of computing ΔW, in which no subtraction of large numbers is involved and which is intrinsically stable at large R. Our method, referred to as the *direct computation* (DC), is based on a formula which represents ΔW as a sum of small contributions which vanish individually at large R when arbitrary bases are used to compute ψ, ϕ_A, and ϕ_B. This formula, given by Eq. (19) of Sec. II, is the main results of our paper. It is derived in Sec. II under the assumption that W is a well-defined Hermitian operator acting in the many-electron Hilbert space. When ψ, ϕ_A, and ϕ_B are computed using the full configuration interaction expansion and a common (dimer-centered) basis set, then Eqs. (1) and (19) give the same result.

One should mention here that two other direct methods of computing ΔW have been used in the literature. One possibility is to generate the expansion of ΔW in powers of $1/R$ (see, e.g., Refs. [12–14]). This expansion, asymptotic in the Poincaré sense, gives very accurate results for very large R, but is inadequate in the important region of the van der Waals well when the exchange and overlap effects are important. Another possibility, proposed by Moszynski and collaborators [14–16], is to use the Hellmann-Feynman theorem and the symmetry-adapted perturbation theory (SAPT) expansion for the interaction energy [17] to develop ΔW as an infinite series in powers of the intermolecular interaction operator. This method does account for the overlap and exchange effects and gives very good results in the region of the van der Waals well [15,16]. It relies, however, on the applicability of the perturbation theory (it has been implemented through second order only) while our formula (19) is nonperturbative and gives the exact result in the limit of a large basis set.

To test our method we used the explicitly correlated Gaussian geminal basis [18] to compute the relativistic mass velocity and one-electron Darwin contributions to the interaction energy of two ground-state hydrogen atoms at separations close to the van der Waals minimum in the triplet state. These two contributions can be defined [19] via Eq. (1) with W replaced by

$$H_{\mathrm{mv}} = -\frac{1}{8}\alpha^2 \sum_i \mathbf{p}_i^4 \tag{4}$$

and

$$D_1 = \frac{\pi}{2}\alpha^2 \sum_n Z_n \sum_i \delta(\mathbf{r}_{in}), \tag{5}$$

respectively, where $\alpha=1/137.036$ is the fine-structure constant, $\mathbf{p}_i$ is the momentum of the ith electron, Z_n is the charge of the nth nucleus, $\mathbf{r}_{in}$ is the distance between the ith electron and the nth nucleus, and $\delta(\mathbf{r})$ is the three-dimensional Dirac distribution. The mass-velocity and one-electron Darwin terms, when added up, represent the so-called Cowan-Griffin approximation [20] to the α^2 relativistic correction to the interaction energy. However, knowledge of the expectation value of D_1 is needed to obtain the α^3, QED contribution to the interaction energy. Therefore we considered the contributions from H_{mv} and D_1 separately, both at finite distances and asymptotically at large interatomic separations R.

These small interaction energy components, considered previously in Refs. [21] and [22], are of interest for contemporary research in the field of ultracold atomic collisions [23,24] since the effects of small contributions to the interaction potential are enhanced by the very low collision energies giving rise to significant corrections to the scattering length [25–27], to the dissociation energies of the long-range, under-threshold states [26,28], or to the binding energies of atomic tritium clusters [29]. It turns out that even when a small molecular system is considered it is not easy to calculate the relativistic corrections to the interaction energy precisely and, as we shall show, the results obtained in Refs. [21] and [22] are not very accurate at large R.

The results of application of our method to the $X\ ^1\Sigma_g^+$ and $b\ ^3\Sigma_u^+$ states of H_2 are reported in Sec. V. For a comparison we also present results obtained with the same basis sets, but using the BF and MC approaches, and, when possible, with the literature data obtained with the Kolos-Wolniewicz basis [30] (exponential functions times polynomials in all interparticle distances). We used an explicitly correlated Gaussian basis set since the applicability of this basis extends also to larger systems [8].

To better assess the accuracy at large interatomic separations we computed appropriate relativistic corrections to dynamic polarizability of hydrogen and obtained the leading terms (through $1/R^{10}$) in the asymptotic $1/R$ expansion of the investigated corrections. The same relativistic dynamic polarizabilities were employed to compute the damping functions [31,32] accounting for the retardation effects. Thus the interaction energy components obtained by us exhibit the correct $1/R^7$ asymptotics and remain accurate at very large interatomic separations R.

It should be noted that the mathematical derivation presented in Sec. II is not valid for the singular operators such as those given in Eqs. (4) and (5). In the Appendix we show that our method—i.e., Eq. (19)—remains valid for such operators provided that the nonlinear parameters are not reoptimized in computing the auxiliary, "first-order" functions appearing in Eq. (19).

Throughout the paper atomic units are used.

II. THEORY

The wave function ψ for an interacting system consisting of subsystems (monomers) A and B is obtained by solving the electronic Schrödinger equation

$$h\psi = e\psi, \tag{6}$$

with the nonrelativistic Hamiltonian

$$h = h_0 + v, \tag{7}$$

where $h_0 = h_A + h_B$ is the sum of the monomer Hamiltonians and v is the interaction operator collecting the Coulomb potentials corresponding to interactions of electrons and nuclei from monomer A with those from monomer B. The functions ϕ_A and ϕ_B appearing in Eq. (1) are eigenfunctions of h_A and h_B, respectively, corresponding to eigenvalues e_A and e_B. The eigenproblem for h_0,

$$h_0\phi = e_0\phi, \tag{8}$$

has a solution $\phi = \phi_A\phi_B$ and $e_0 = e_A + e_B$. We assume that the eigenvalues e, e_A, and e_B are nondegenerate or can be treated as nondegenerate by restricting our attention to a particular representation of the common symmetry group of h, h_A, and h_B.

We introduce a formal expansion parameter λ and define the perturbed Hamiltonian

$$H(\lambda) = h + \lambda W. \tag{9}$$

The operator W can be split, in a manner similar to that of Eq. (7), as $W = W_0 + U$, where $W_0 = W_A + W_B$ is the intramonomer part of W and $U = W - W_0$ is the interaction contribution. The whole perturbed Hamiltonian $H(\lambda)$ can hence be divided into its intramonomer and interaction parts:

$$H(\lambda) = H_0(\lambda) + V(\lambda), \tag{10}$$

where

$$H_0(\lambda) = h_0 + \lambda W_0 \tag{11}$$

and

$$V(\lambda) = v + \lambda U. \tag{12}$$

We shall assume that the eigenfunctions and eigenvalues of $H(\lambda)$ and $H_0(\lambda)$, defined by

$$(h + \lambda W)\Psi(\lambda) = E(\lambda,R)\Psi(\lambda) \tag{13}$$

and

$$(h_0 + \lambda W_0)\Phi(\lambda) = E_0(\lambda)\Phi(\lambda), \tag{14}$$

exist for sufficiently small λ and have power series expansions around $\lambda = 0$. This happens when the operator W is Hermitian on a dense domain and bounded relative to h [33]. This condition is fulfilled by the operators used in the Appendix to regularize the relativistic perturbations of Eqs. (4) and (5). Perturbations describing interactions with an external electromagnetic fields are not bounded relative to h, but are usually less singular than those of Eqs. (4) and (5). They can be treated using a regularization similar to that applied in the Appendix. All eigenfunctions in Eqs. (6), (8), (13), and (14) depend also parametrically on R, but the information on this dependence is suppressed for notational brevity. We pick up those solutions of Eqs. (13) and (14) which approach ψ and ϕ when $\lambda \to 0$—i.e., satisfy $\Psi(0) = \psi$ and $\Phi(0) = \phi$. We shall have to differentiate $\Psi(\lambda)$ and $\Phi(\lambda)$, so we assume that these eigenfunctions are unique (i.e., nondegenerate after resolving possible symmetries) when a normalization is fixed. To make our notation more transparent the wave functions and operators dependent on the perturbation W or W_0 are always denoted by uppercase letters while those independent of these perturbations by lowercase letters. The wave functions dependent on the interaction operators v or U are denoted by ψ or Ψ and those independent of those operators (describing noninteracting monomers) by ϕ or Φ.

Applying the Hellmann-Feynman theorem to Eqs. (9) and (11) one can express the expectation values entering Eq. (1) through the eigenvalues of $H(\lambda)$ and $H_0(\lambda)$:

$$\langle\psi|W|\psi\rangle = \left.\frac{\partial E(\lambda,R)}{\partial\lambda}\right|_{\lambda=0} \tag{15}$$

and

$$\langle\phi_A|W_A|\phi_A\rangle + \langle\phi_B|W_B|\phi_B\rangle = \langle\phi|W_0|\phi\rangle = \left.\frac{\partial E_0(\lambda)}{\partial\lambda}\right|_{\lambda=0}. \tag{16}$$

Subtracting Eq. (16) from Eq. (15) we find that

$$\Delta W = \left.\frac{\partial[E(\lambda,R) - E_0(\lambda)]}{\partial\lambda}\right|_{\lambda=0}. \tag{17}$$

The difference $E(\lambda,R) - E_0(\lambda)$ can be computed directly from the equation

$$E(\lambda,R) - E_0(\lambda) = \frac{\langle\Phi(\lambda)|v + \lambda U|\Psi(\lambda)\rangle}{\langle\Phi(\lambda)|\Psi(\lambda)\rangle}, \tag{18}$$

which can be easily proved by projecting Eq. (13) against $\Phi(\lambda)$, replacing $h + \lambda W$ by $h_0 + \lambda W_0 + v + \lambda U$, and using Eq. (14).

Straightforward differentiation of the rhs of Eq. (18) leads (after setting $\lambda = 0$) to

$$\Delta W = \frac{1}{\langle\phi|\psi\rangle}[\langle\phi|U|\psi\rangle + \langle\Phi_1|v - e_1|\psi\rangle + \langle\phi|v - e_1|\Psi_1\rangle], \tag{19}$$

where e_1 is the interaction energy of monomers,

$$e_1 = e - e_0 = \frac{\langle\phi|v|\psi\rangle}{\langle\phi|\psi\rangle}, \tag{20}$$

while $\Psi_1 = (\partial\Psi/\partial\lambda)_{\lambda=0}$ and $\Phi_1 = [\partial\Phi(\lambda)/\partial\lambda]_{\lambda=0}$.

The derivative functions Ψ_1 and Φ_1 can be obtained from the Rayleigh-Schrödinger perturbation theory as the first-order corrections to ψ and ϕ due to the perturbations W and W_0, respectively. They satisfy the equations

$$(h-e)\Psi_1 = (\mathcal{E}_1 - W)\psi \tag{21}$$

and

$$(h_0-e_0)\Phi_1 = (\mathcal{E}_0 - W_0)\phi, \tag{22}$$

where $\mathcal{E}_1 = (\partial E/\partial \lambda)_{\lambda=0} = \langle\psi|W|\psi\rangle$ and $\mathcal{E}_0 = (\partial E_0/\partial \lambda)_{\lambda=0} = \langle\phi|W_0|\phi\rangle$. Equation (22) is separable, and its solution can be written in the form

$$\Phi_1 = \phi_A \Phi_B + \Phi_A \phi_B, \tag{23}$$

where Φ_X, $X=A,B$, satisfies the single-monomer equation $(h_X - e_X)\Phi_X = (E_X - W_X)\Phi_X$, with $\mathcal{E}_X = \langle\phi_X|W_X|\phi_X\rangle$.

One can verify that each of the functions $U\phi$, $v\Phi_1$, and $v\phi$ as well as the interaction energy e_1 itself vanish at infinite intermonomer separation. Thus each of the individual contributions in Eq. (19) goes to zero at large R and this property holds for any basis employed to represent the wave functions appearing in Eq. (19). Note that the function Ψ_1, defined by Eq. (21), does not grow with increasing R even if ψ is asymptotically degenerate at infinite R since the excited, asymptotically degenerate states differ from ψ by symmetry and do not contribute to Ψ_1.

Since the operators $h-e$ and $h_X - e_X$ are positive definite, the solutions of Eqs. (21) and (22) can be conveniently obtained by expanding Ψ_1 and Φ_1 in a suitable basis set and optimizing both linear and nonlinear parameters using the Hylleraas variational principle. This procedure is justified if $W\psi$ and $W_0\phi$ are well-defined square-integrable functions belonging to the domain of h and h_0, respectively. This condition is obviously not fulfilled by highly singular perturbations like those given in Eqs. (4) and (5). We show in the Appendix that Eq. (19) gives correct results also for such operators provided that the Hylleraas variational procedure of solving Eqs. (21) and (22) involves the linear minimization only.

III. ASYMPTOTIC BEHAVIOR OF THE COWAN-GRIFFIN CONTRIBUTION TO THE INTERACTION ENERGY

To assess the accuracy of our method at large interatomic separations R and to provide an asymptotically correct analytical fit of the Cowan-Griffin contribution to the interaction energy, we computed constants determining the large-R behavior of the mass-velocity and one-electron Darwin relativistic corrections defined via Eq. (1) with W replaced by the operators H_{mv} and D_1 of Eqs. (4) and (5). It is well known that at large interatomic distances the nonrelativistic interaction energy of spherically symmetric atoms can be expanded as an asymptotic series in negative powers of R:

$$E_{\mathrm{int}}(R) = -C_6 R^{-6} - C_8 R^{-8} - C_{10} R^{-10} + O(R^{-11}). \tag{24}$$

One can easily show that the relativistic corrections considered by us can be expanded in a similar way:

$$\Delta W = -\delta C_6 R^{-6} - \delta C_8 R^{-8} - \delta C_{10} R^{-10} + O(R^{-11}), \tag{25}$$

where δC_n are constants of the order of α^2. Note that some contributions to the interaction energy predicted by the Breit-Pauli Hamiltonian decay less rapidly than $1/R^6$ and cannot be represented by Eq. (25).

For $n \leq 10$ the nonrelativistic C_n coefficients can be obtained from the atomic polarizabilities computed at imaginary frequencies [34]:

$$C_6 = \frac{3}{\pi} G(1,1), \tag{26}$$

$$C_8 = \frac{15}{\pi} G(1,2), \tag{27}$$

$$C_{10} = \frac{28}{\pi} G(1,3) + \frac{35}{\pi} G(2,2), \tag{28}$$

where

$$G(k,l) = \int_0^\infty \alpha_k(i\omega)\alpha_l(i\omega)d\omega. \tag{29}$$

We assumed here that the interacting atoms are identical and are in the same quantum state. In Eq. (29), $\alpha_l(i\omega)$ denotes the 2^l-pole dynamic polarizability defined as

$$\alpha(i\omega) = \langle\phi_A|Q_{l0}\mathcal{R}(i\omega)Q_{l0}|\phi_A\rangle + \text{c.c.}, \tag{30}$$

where Q_{lm} is the electric 2^l-pole moment operator,

$$Q_{lm} = \sqrt{\frac{4\pi}{2l+1}} \sum_j r_j^l Y_{lm}(\hat{\mathbf{r}}_j), \tag{31}$$

and $\mathcal{R}(i\omega)$ stands for the resolvent $p_A(h_A - e_A + i\omega)^{-1}$, $p_A = 1 - |\phi_A\rangle\langle\phi_A|$ being the projector on the space of excited eigenfunctions of h_A.

It has been shown in Ref. [31] that the three leading coefficients in the asymptotic expansion of Eq. (25) can be expressed via atomic polarizabilities and the leading corrections to these polarizabilities induced by the perturbation W_A. Specifically, the coefficients δC_n, $n \leq 10$, can be obtained from Eqs. (26)–(28) provided that the $G(k,l)$ integrals are replaced by the integrals

$$\delta G(k,l) = \int_0^\infty [\alpha_k(i\omega)\delta\alpha_l(i\omega) + \alpha_l(i\omega)\delta\alpha_k(i\omega)]d\omega, \tag{32}$$

where $\delta\alpha_l(i\omega)$ is the correction to the 2^l-pole polarizability induced by the perturbation W_A (in our case by the H_{mv} or the D_1 operator):

$$\begin{aligned}\delta\alpha_l(i\omega) = &-\langle\phi_A|Q_{l0}\mathcal{R}(i\omega)(W_A - \langle W_A\rangle)\mathcal{R}(i\omega)Q_{l0}|\phi_A\rangle \\ &- 2\langle\phi_A|Q_{l0}\mathcal{R}(i\omega)Q_{l0}\mathcal{R}_0 W_A|\phi_A\rangle + \text{c.c.},\end{aligned} \tag{33}$$

with $\mathcal{R}_0$ standing for $\lim_{\omega\to 0}\mathcal{R}(\omega)$.

We computed the polarizabilities entering Eq. (32) employing the Hylleraas variational principle to obtain the first-order perturbed function $\mathcal{R}(i\omega)Q_{l0}\phi_A$ and the second-order

TABLE I. $1/R$ expansion coefficients for the mass-velocity and Darwin relativistic corrections to the ground-state potential of H_2. The terms $\delta C_{10}^{\mathrm{q-q}}$ and $\delta C_{10}^{\mathrm{d-o}}$ represent quadrupole-quadrupole and dipole-octupole contributions to δC_{10}, respectively. The sum of those terms gives the total δC_{10}.

	H_{mv}	D_1
$\delta C_6/\alpha^2$	−46,6002853381	34,685544399
$\delta C_8/\alpha^2$	−1107,27044690	824,58297664
$\delta C_{10}^{\mathrm{q-q}}/\alpha^2$	−12112,4495896	9031,1335032
$\delta C_{10}^{\mathrm{d-o}}/\alpha^2$	−22427,22527	16914,43043

one $\mathcal{R}_0 Q_{l0} \mathcal{R}(i\omega) Q_{l0} \phi_A$. The radial parts of trial functions were expanded as polynomials in r times a single exponential with an exponent optimized at $\omega=0$. This exponent was not reoptimized when computing the second-order function. Polynomials up to 256th order were used (multiple-precision arithmetic was applied), although after performing these calculations we found that somewhat shorter, 160-term expansions would be sufficient for the level of precision presented in Table I. All figures shown in this table appear to be converged. The δC_6 constant corresponding to the D_1 perturbation was obtained earlier by Jamieson, Dalgarno, and Wolniewicz [22] using a different computational procedure. Their value of $\delta C_6(D_1)/\alpha^2$, equal to $28.29\alpha^2$, differs significantly from the result of present calculation given in Table I and equal to 34.6855…. The reason for this disagreement is not clear to us. We verified, however, that our value agrees much better with the finite-R results presented in Sec. V and with data computed independently by Przybytek [35].

The known values of δC_n allow us to construct asymptotically correct analytical fits of the relativistic corrections computed at finite distances. We provide fits for both the total Cowan-Griffin energy and for its one-electron Darwin part since the latter is needed to compute the α^3, Lamb-shift contribution to the interaction energy. We found it sufficient to use a relatively simple function depending on three nonlinear (α, β, and η) and two (triplet-state) and six or seven (singlet-state) linear parameters $(A_0, \dots, A_6)$:

$$\Delta W(R) = e^{-\alpha R^2 - \beta R} \sum_{k=0} A_k R^k - \sum_{n=6,8,10} f_n(\eta R) \frac{\delta C_n}{R^n}, \quad (34)$$

where $f_n(x) = 1 - e^{-x}(1 + x + x^2/2! + \cdots + x^n/n!)$ is the Tang-Toennies [36] damping function. The fit of the relativistic corrections to the energy of the $b\,{}^3\Sigma_u^+$ state was obtained using our data points exclusively (eight equally spaced points between $R=5.0$ bohrs and $R=12$ bohrs), and since no points were computed for $R<5$ bohrs, it cannot be reliably used for shorter distances. In the case of the fit of the relativistic corrections to the energy of the ground, $X\,{}^1\Sigma_g^+$ state, our values were used for $R \geq 5$ bohrs and the published results of Wolniewicz [21] were adopted for $R<5$ bohrs. This fit is therefore valid also in the chemical minimum region and for R as small as 0.6 bohr. The singlet fits for both one-electron Darwin and Cowan-Griffin corrections give errors smaller than 3% for all interatomic distances, while triplet fits give errors smaller than 2% or 5% in the case of one-electron Darwin and Cowan-Griffin corrections, respectively. All fit parameters are given in Table II.

It is well known that Eq. (34) cannot correctly represent the relativistic part of the interaction energy at very large R. As a result of the retardation of electromagnetic interactions, the interaction energy between neutral atoms falls off as R^{-7} for R larger than the wavelength corresponding to the average atomic excitation energy [37]. The same retardation damping influences the Cowan-Griffin contributions to the interaction energy. According to the relativistic generalization of the Casimir-Polder theory [31,32] the mass-velocity and one-electron Darwin terms are damped at large R according to the following *switching function* (from R^{-6} to R^{-7}):

$$\Delta W_{\mathrm{CP}}(R) = -\frac{2}{\pi R^6} \int_0^\infty \alpha_1(i\omega)\, \delta\alpha_1(i\omega)\, e^{-2\omega R \alpha} P(\omega R \alpha)\, d\omega, \quad (35)$$

where $P(x) = x^4 + 2x^3 + 5x^2 + 6x + 3$. Using the computed values of $\alpha_1(i\omega)$ and $\delta\alpha_1(i\omega)$ we evaluated Eq. (35) for a wide

TABLE II. Fit parameters for the Cowan-Griffin and Darwin relativistic corrections to the potential energy curves of the $X\,{}^1\Sigma_g^+$ and $b\,{}^3\Sigma_u^+$ states of H_2.

	Singlet		Triplet	
	H_{CG}	D_1	H_{CG}	D_1
η	3,2240848630	1,8119548084	1,4391114051	1,2433907106
α	0,0139216369	0,0807340145	0,0426274892	0,0489429063
β	1,9846801684	0,9482917942	0,7753660481	0,6231832266
A_0	−3,5520673072	9,1015168917	−0,8951390715	1,0973431033
A_1	−114,4209333380	−11,3897287746	0,0824707410	−0,1019331893
A_2	101,6653888345	8,3552717753		
A_3	−44,4601360103	−3,1599596525		
A_4	10,8428717265	0,4930955043		
A_5	−1,2530014130	−0,0281535413		
A_6	0,0571850859			

TABLE III. Fit parameters for the retardation damping functions, Eq. (37), corresponding to the "nonrelativistic" Casimir-Polder energy, $g_0(x)$, to the Cowan-Griffin correction, $g_2(x)$, and to one-electron Darwin, $g_{D1}(x)$, relativistic corrections for the $X\ {}^1\Sigma_g^+$ and $b\ {}^3\Sigma_u^+$ states of H_2.

	$g_0(R)$	$g_{D_1}(R)$	$g_2(R)$
a_2	0.0852707493	0.0385312061	0.0734452185
a_3	0.0027739117	0.0016078309	0.0021816008
b_1	0.7981387616	0.4165462412	0.7538308635
b_2	0.1532803616	0.0664522585	0.1283453068
b_3	0.0149724066	0.0052372139	0.0114005996
b_4	0.0004863867	0.0002184200	0.0003381225

range of R values and fitted it very accurately to the rational function

$$\Delta W_{\mathrm{CP}}(R) = -\,\delta C_6 R^{-6} g_2(\alpha R), \tag{36}$$

where

$$g_2(x) = \frac{1 + b_1 x + a_2 x^2 + a_3 x^3}{1 + b_1 x + b_2 x^2 + b_3 x^3 + b_4 x^4}. \tag{37}$$

The coefficients a_i and b_i, optimized to reproduce the rhs of Eq. (35) with a relative error smaller than 10^{-4}, are presented in Table III together with similar coefficients needed to fit the conventional "nonrelativistic" Casimir-Polder interaction energy [given by Eq. (35) with $\delta\alpha_1$ replaced by $\alpha_1/2$] with the function $E_{\mathrm{CP}}(R) = -C_6 R^{-6} g_0(\alpha R)$. In Table III we also list the coefficients, denoted by g_{D1}, describing the retardation of the Darwin part of the Cowan-Griffin (CG) energy [defined via Eqs. (35)–(37) with the polarizability correction $\delta\alpha_1(i\omega)$ replaced by its Darwin component], since these coefficients are needed to correctly eliminate the unphysical $1/R^6$ decay of the α^3 (Lamb-shift) contribution to the interaction energy.

Using Eq. (35) or (36) for R larger than a certain splicing distance R_s and Eq. (34) for R smaller than R_s is not convenient since such a procedure would be ambiguous (there is no natural choice of R_s) and the resulting potential would be nonanalytic. Therefore we propose to use an additive retardation correction to Eq. (34), consistent with Eq. (35) and free from the problems mentioned above. To obtain this correction we note that the expansion of $\Delta W_{\mathrm{CP}}(R)$ in powers of the fine-structure constant α has the form

$$\Delta W_{\mathrm{CP}}(R) = -\,\delta C_6 R^{-6} + O(\alpha^4), \tag{38}$$

where the first term is of the order of α^2 and the term denoted by $O(\alpha^4)$ collects contributions of the fourth and higher order in α. Equation (35) may be viewed as a selective summation of certain QED terms up to infinite order in α. What is new in comparison with Eq. (34), which itself is of the second order in α, are the α^4 and higher-order terms given by $\Delta W_{\mathrm{CP}}(R) + \delta C_6 R^{-6}$. These terms represent the needed additive retardation correction

$$\delta W_{\mathrm{ret}} = [1 - g_2(\alpha R)]\delta C_6 R^{-6} \tag{39}$$

to be added to Eq. (34) to remove the unphysical R^{-6} decay of $\Delta W(R)$. To avoid some loss of accuracy arising when δW_{ret} is added to $\Delta W(R)$ at large R, we propose that only $-g_2(\alpha R)\delta C_6 R^{-6}$—i.e., the whole $\Delta W_{\mathrm{CP}}(R)$ term of Eq. (36)—is added to $\Delta W(R)$ and the addition of $\delta C_6 R^{-6}$ is taken care of by replacing the damping function $f_6(x)$ in Eq. (34) with $f_6(x) - 1 = (1 + x + x^2/2! \cdots x^6/6!)e^{-x}$. The resulting contribution to the interatomic potential is now unambiguous and remains analytic at all values of R greater than $R = 0$.

IV. COMPUTATIONAL DETAILS

We have performed calculations of the mass-velocity and one-electron Darwin contributions to the interaction energy of hydrogen atoms in the lowest singlet ($X\ {}^1\Sigma_g^+$) and triplet ($b\ {}^3\Sigma_u^+$) electronic states. For each interatomic separation considered by us, the spatial part of the nonrelativistic wave function ψ was represented as an expansion in the basis of Gaussian geminals of the form

$$\eta_i = (1 \pm I)(1 \pm P)\exp(-\,\alpha_i r_{1A}^2 - \alpha_i' r_{2A}^2 \\ -\,\beta_i r_{1B}^2 - \beta_i' r_{2B}^2 - \gamma_i r_{12}^2), \tag{40}$$

where r_{kC} is the distance between the electron k and nucleus C and r_{12} is the interelectronic separation. The operator P stands for the permutation of electrons and I for the inversion through the center of the dimer. The sign + is used for the singlet and − for triplet state. When the exponents α_i, α_i', β_i, β_i', and γ_i are not constrained and assume different values for different i, then the basis given in Eq. (40) is complete in the uniform convergence [38] and the Sobolev space [39] topologies, which guarantees that the basis set (40) can be used in a computation of the expectation value of the Dirac distribution.

To describe correctly the dissociation into the 1*s* atomic states of hydrogen, we have also added to our basis set the Heitler-London function

$$\psi_0 = (1 \pm P)\phi_{1s}(r_{1A})\phi_{1s}(r_{2B}). \tag{41}$$

The ϕ_{1s} orbital in the above function was approximated by a contraction of 25 primitive Gaussian functions with exponents carefully optimized on the ground-state energy of the hydrogen atom.

For each interatomic distance all exponents α_i, α_i', β_i, β_i', and γ_i in all η_i functions were variationally optimized on the total nonrelativistic energy of the dimer. The optimization procedure was performed in the presence of the "frozen" ψ_0 function. Three basis sets, composed of 128, 256, and 512 geminal functions, were obtained in this way, These bases will be referred to as B128, B256, and B512, respectively. The nonrelativistic interaction energies resulting from this optimization are given in Tables IV and V. For the singlet state our energies are practically as good as the best published data—also shown in the tables. For the triplet state and the van der Waals minimum region, our energies appear to be the most accurate to date.

TABLE IV. Nonrelativistic interaction energies for the $X\,^1\Sigma_g^+$ state of H_2 (in millihartree).

R	Basis 128	Basis 256	Basis 512	Ref. [22]
5	−3.7856033	−3.7856480	−3.7856532	−3.785656
6	−0.8356870	−0.8357017	−0.8357037	−0.835707
7	−0.1979021	−0.1979081	−0.1979128	−0.197914
8	−0.0555937	−0.0556002	−0.0556042	−0.055605
9	−0.0197788	−0.0197805	−0.0197814	−0.019782
10	−0.0087549	−0.0087553	−0.0087555	−0.008755
11	−0.0045051	−0.0045057	−0.0045059	−0.004506
12	−0.0025458	−0.0025458	−0.0025458	−0.002546

TABLE V. Nonrelativistic interaction energies for the $b\,^3\Sigma_u^+$ state of H_2 (in millihartree).

R	Basis 128	Basis 256	Basis 512	Ref. [22]
5	1.3127756	1.3127477	1.3127452	1.312747
6	0.1865612	0.1865534	0.1865521	0.186553
7	−0.0040028	−0.0040047	−0.0040052	−0.003987
8	−0.0202194	−0.0202208	−0.0202209	−0.020214
9	−0.0135166	−0.0135169	−0.0135175	−0.013517
10	−0.0076733	−0.0076736	−0.0076738	−0.007674
11	−0.0043228	−0.0043228	−0.0043229	−0.004323
12	−0.0025153	−0.0025154	−0.0025154	−0.002515

V. NUMERICAL RESULTS AND DISCUSSION

We present the results of three types of calculations. The first one, referred as the BF calculation, is based on Eq. (1) with the exact atomic values subtracted. The second one, referred as the MC scheme, is defined precisely in Sec. I; cf. the paragraph containing Eqs. (2) and (3). In the MC approach all nonlinear parameters are optimized in the presence of the "zeroth-order function" ψ_0. The third one, referred as the DC, amounts to computing the expression (19).

The results obtained for the D_1 and H_{mv} corrections to the interaction potential of the $X\,^1\Sigma_g^+$ state of H_2 are collected in Tables VI and VII, respectively. The results for the $b\,^3\Sigma_u^+$ state are given in Table VIII (Darwin correction) and Table IX (mass-velocity correction).

The behavior of the obtained results is very similar in all four cases. For all interatomic separations and all basis sets, results coming from the MC and DC calculations are fully consistent. The difference between them is usually negligible and in only very few instances exceeds 0.1%. This agreement appears to be independent of the size of the employed

TABLE VI. One-electron Darwin correction to the interaction energy of the $^1\Sigma_g^+$ state (in α^2 × millihartree).

R	Method	Basis 128	Basis 256	Basis 512	Ref. [21]	Ref. [22]
5	BF	−19.5014	−19.4127	−19.4070	−19.197	−19.207
	MC	−19.3242	−19.2355	−19.2298		
	DC	−19.3242	−19.2355	−19.2298		
6	BF	−5.3701	−5.3841	−5.3674	−5.162	−5.161
	MC	−5.1929	−5.2069	−5.1902		
	DC	−5.1929	−5.2069	−5.1906		
7	BF	−1.5340	−1.5333	−1.5339	−1.357	−1.351
	MC	−1.3568	−1.3561	−1.3567		
	DC	−1.3568	−1.3561	−1.3567		
8	BF	−0.56224	−0.56059	−0.56426	−0.393	−0.383
	MC	−0.38503	−0.38338	−0.38705		
	DC	−0.38505	−0.38338	−0.38706		
9	BF	−0.30943	−0.30822	−0.30653	−0.126	−0.129
	MC	−0.13222	−0.13101	−0.12932		
	DC	−0.13222	−0.13083	−0.12932		
10	BF	−0.23305	−0.23093	−0.23067	−0.057	−0.052
	MC	−0.05583	−0.05372	−0.05346		
	DC	−0.05584	−0.05370	−0.05346		
11	BF	−0.20417	−0.20223	−0.20311	−0.023	−0.025
	MC	−0.02696	−0.02502	−0.02590		
	DC	−0.02697	−0.02505	−0.02588		
12	BF	−0.19481	−0.19117	−0.19167	−0.012	−0.014
	MC	−0.01760	−0.01396	−0.01446		
	DC	−0.01760	−0.01398	−0.01446		

TABLE VII. Mass-velocity correction to the interaction energy in the $^1\Sigma_g^+$ state (in $\alpha^2\times$millihartree).

R	Method	Basis 128	Basis 256	Basis 512	Ref. [21]
5	BF	27.5334	27.3692	27.3582	27.138
	MC	27.3562	27.1919	27.1810	
	DC	27.3562	27.1919	27.1809	
6	BF	7.3125	7.3410	7.3097	7.075
	MC	7.1353	7.1638	7.1325	
	DC	7.1353	7.1638	7.1397	
7	BF	2.0069	2.0051	2.0068	1.816
	MC	1.8296	1.8279	1.8296	
	DC	1.8296	1.8265	1.8296	
8	BF	0.69193	0.68862	0.69605	0.512
	MC	0.51471	0.51140	0.51882	
	DC	0.51475	0.51140	0.51925	
9	BF	0.35581	0.35340	0.35001	0.170
	MC	0.17859	0.17617	0.17278	
	DC	0.17859	0.17618	0.17277	
10	BF	0.25374	0.24950	0.24899	0.072
	MC	0.07651	0.07227	0.07177	
	DC	0.07651	0.07224	0.07177	
11	BF	0.21404	0.21015	0.21189	0.034
	MC	0.03682	0.03293	0.03467	
	DC	0.03684	0.03299	0.03470	
12	BF	0.20302	0.19575	0.19674	0.019
	MC	0.02580	0.01853	0.01952	
	DC	0.02580	0.01858	0.01952	

TABLE VIII. One-electron Darwin correction to the interaction energy in the $^3\Sigma_u^+$ state (in $\alpha^2\times$millihartree).

R	Method	Basis 128+	Basis 256+	Basis 512+	Ref. [22]
5	BF	6.0489	6.0185	6.0265	6.203
	MC	6.2262	6.1957	6.2038	
	DC	6.2262	6.1957	6.2037	
6	BF	1.1165	1.1271	1.1263	1.321
	MC	1.2938	1.3043	1.3035	
	DC	1.2938	1.3043	1.3034	
7	BF	−0.0587	−0.0567	−0.0556	0.101
	MC	0.1186	0.1205	0.1213	
	DC	0.1186	0.1205	0.1213	
8	BF	−0.25207	−0.25000	−0.25069	−0.075
	MC	−0.07486	−0.07279	−0.07348	
	DC	−0.07486	−0.07280	−0.07348	
9	BF	−0.24354	−0.24489	−0.24375	−0.060
	MC	−0.06633	−0.06768	−0.06654	
	DC	−0.06633	−0.06768	−0.06654	
10	BF	−0.21704	−0.21520	−0.21923	−0.040
	MC	−0.03983	−0.03799	−0.04202	
	DC	−0.03982	−0.03798	−0.04200	
11	BF	−0.20014	−0.20066	−0.20093	−0.025
	MC	−0.02293	−0.02345	−0.02372	
	DC	−0.02317	−0.02347	−0.02372	
12	BF	−0.19061	−0.19126	−0.19126	−0.014
	MC	−0.01340	−0.01405	−0.01404	
	DC	−0.01344	−0.01404	−0.01404	

basis set and does not deteriorate at larger R, despite the fact that the calculated corrections become then rather small in absolute value. The observed agreement confirms the soundness of the MC procedure. In contrast, the results obtained in the BF calculations differ significantly from the DC and MC results. The difference increases dramatically with the interatomic separation. For $R=5$ bohrs the difference between the BF and DC calculations varies from only about 0.6% (for the H_{mv} correction to singlet state) to about 3% (for the D_1 correction to triplet state), but for the largest considered intermolecular separation ($R=12$ bohrs) the BF and DC results differ by one order of magnitude.

Tables VI–VIII list also the results of earlier calculations by Wolniewicz [21] and by Jamieson *et al.* [22] performed using the Kolos-Wolniewicz basis [30] and the BF approach. The BF approach is this case accurate at large R since the Kolos-Wolniewicz basis includes the exact, nonexpanded, asymptotic function ψ_0. Our results agree better with the later, more accurate calculations of Ref. [22]. We believe that at larger R our calculations are more accurate than those of Refs. [21] and [22] since they agree somewhat better with the asymptotic expansion of the relativistic corrections, *vide infra*.

To examine the accuracy of the interaction energies at larger values of R, we plotted the values of $R^6\alpha^{-2}\Delta W(R)$ for various approximations to the corrections $\Delta W(R)$ and compared the results with the plot of the function

$$-\delta C_6\alpha^{-2}-\delta C_8\alpha^{-2}R^{-2}-\delta C_{10}\alpha^{-2}R^{-4}, \tag{42}$$

where δC_n, $n=6,8,10$, are the coefficients (given in Table I) determining the asymptotic behavior of the Darwin or mass-velocity contributions. Figures 1–4 present results of this comparison. It is clearly seen that the BF method fails dramatically at the distances of the van der Waals minimum and that the MC and DC methods give practically identical results. The results obtained using the Kolos-Wolniewicz basis [21,22], when available, are similar to our results, although the differences are visible. The most significant difference is observed for the Darwin correction in the singlet state when the results from Ref. [21] start to deviate from the exact asymptotics at the largest values of R. Figure 1 shows also that our value of the constant $\delta C_6(\text{D}_1)/\alpha^2=34.6855\ldots$, given in Table I, is more consistent with the finite-R results than the value 28.29 obtained in Ref. [22].

To show that the agreement between the MC and DC values is not trivial in Figs. 1 and 2, we present also results obtained with a simplified MC procedure, denoted by MC*, in which the ψ_0 function is added to a previously optimized geminal basis set. As this previously optimized basis set, we used a very carefully optimized 1200-term Gaussian geminal

TABLE IX. Mass-velocity correction to the interaction energy in the $^3\Sigma_u^+$ state (in $\alpha^2 \times$millihartree).

R	Method	Basis 128	Basis 256	Basis 512
5	BF	−8.7988	−8.7339	−8.7494
	MC	−8.9760	−8.9111	−8.9267
	DC	−8.9761	−8.9112	−8.9266
6	BF	−1.6130	−1.6339	−1.6323
	MC	−1.7902	−1.8111	−1.8095
	DC	−1.7902	−1.8111	−1.8101
7	BF	0.0224	0.0186	0.0170
	MC	−0.1548	−0.1587	−0.1602
	DC	−0.1548	−0.1587	−0.1602
8	BF	0.28384	0.27971	0.28109
	MC	0.10662	0.10249	0.10387
	DC	0.10661	0.10249	0.10388
9	BF	0.26793	0.27063	0.26834
	MC	0.09070	0.09340	0.09111
	DC	0.09070	0.09341	0.09108
10	BF	0.23042	0.22674	0.23477
	MC	0.05320	0.04951	0.05754
	DC	0.05319	0.04868	0.05748
11	BF	0.20763	0.20865	0.20920
	MC	0.03040	0.03143	0.03197
	DC	0.03090	0.03146	0.03173
12	BF	0.19495	0.19624	0.19623
	MC	0.01773	0.01902	0.01900
	DC	0.01780	0.01899	0.01900

basis for the singlet state provided to us by Cencek [40]. This basis set gives subnanohartree accuracy at each value of R—i.e., gives significantly more accurate nonrelativistic interaction energies than our largest 512-term basis. The results obtained when this 1200-term basis is extended with the Gaussian representation of ψ_0 function used in our work are shown in Figs. 1 and 2 (the MC* results). Despite the high quality of the original basis, these results are seen to be very poor at larger values of R. This clearly demonstrates that it is critically important to optimize the nonlinear parameters with the "zeroth-order" function ψ_0 included. This conclusion agrees with the observation made in Ref. [9].

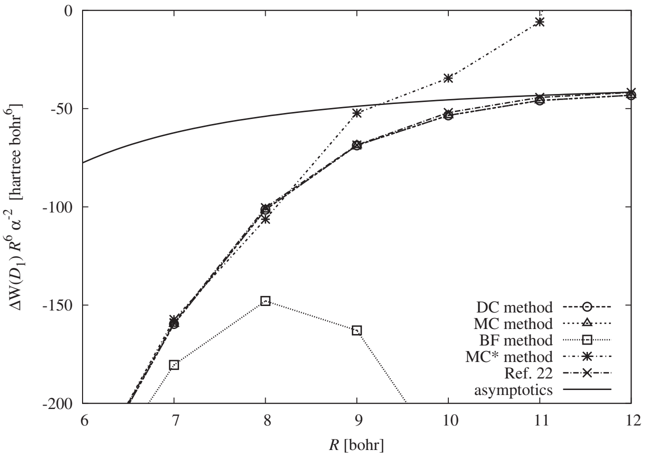

FIG. 1. Asymptotic behavior of D_1 correction to the interaction energy of the $^1\Sigma_g^+$ state obtained with a set of 512 basis functions.

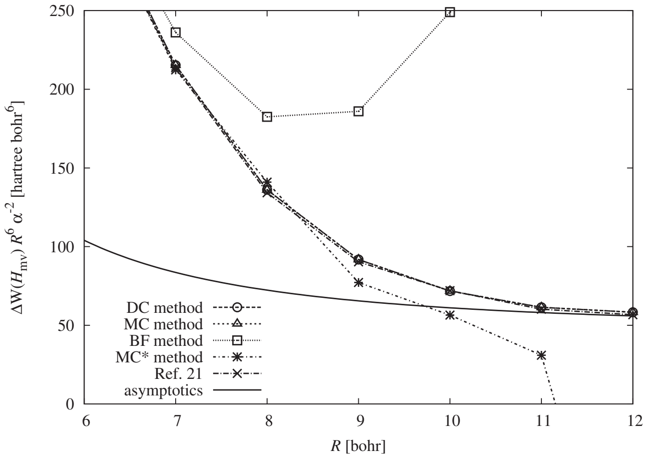

FIG. 2. Asymptotic behavior of $H_{\rm mv}$ correction to the interaction energy of the $^1\Sigma_g^+$ state obtained with a set of 512 basis functions.

As can be seen in Tables VI and IX, the basis-set convergence is not monotonic. This prevented us from using a basis-set extrapolation to obtain recommended values of the CG relativistic energies. Therefore, we used the values computed with the largest, 512-term basis to obtain our analytical fits, Eq. (34). We estimate that our fitting functions, defined by the parameters given in Table II, represent the exact α^2 relativistic corrections with errors smaller than 0.1% at small R and reaching up to about 1% at the distances of the attractive part of the van der Waals minimum. At still larger distances the errors decrease because of the practically exact form of the asymptotic expansion used in Eq. (34).

VI. SUMMARY

We proposed a method to directly compute the interaction-induced properties for weakly interacting monomers.

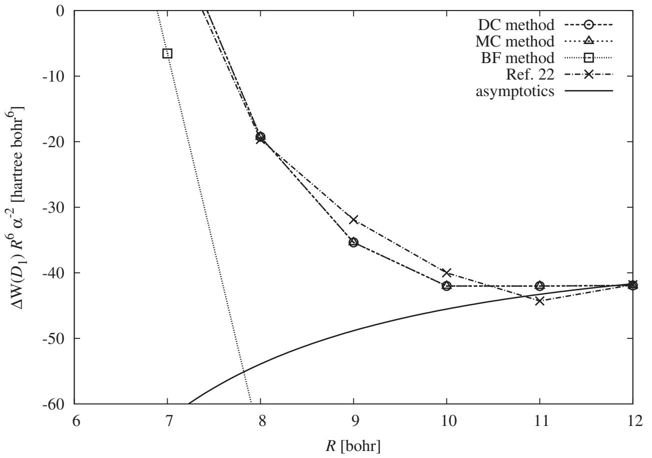

FIG. 3. Asymptotic behavior of D_1 correction to the interaction energy of the $^3\Sigma_u^+$ state obtained with a set of 512 basis functions.

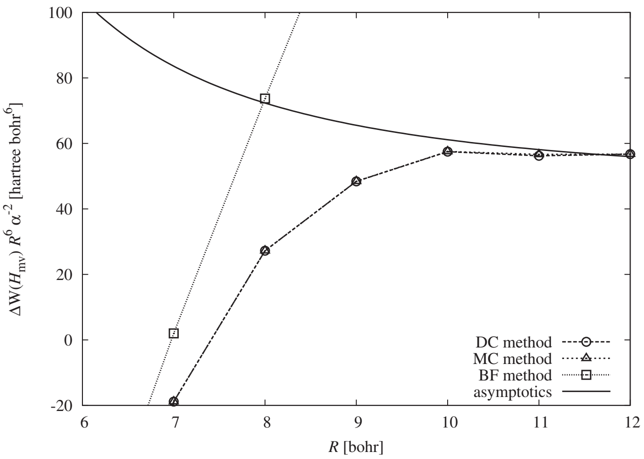

FIG. 4. Asymptotic behavior of H_{mv} correction to the interaction energy of the $^3\Sigma_u^+$ $^3\Sigma_u^+$ state obtained with a set of 512 basis functions.

We applied it in Gaussian geminal calculations of the Cowan-Griffin relativistic corrections to the interaction energy in the ground singlet and the lowest triplet states of the hydrogen molecule. The proposed method gives results which are very close to those obtained using the so-called monomer contraction method proposed recently by Cencek and collaborators [9], confirming thereby the validity of the latter method.

To assess the accuracy of the obtained relativistic corrections, we computed the constants determining their large-R asymptotic behavior. These constants were used to obtain an analytic fit representing the computed corrections and valid in a wide range of interatomic distances. To extend the validity of this analytical fit to very large interatomic separations, we computed the damping functions accounting for the retardation and producing the correct $1/R^7$ decrease of the interaction energy.

Is should be pointed out that the proposed method can be used not only to calculate corrections coming from relativistic operators, but also, in a more general context, to obtain arbitrary first-order molecular properties of weakly interacting atoms.

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APPENDIX

In this appendix we prove the validity of Eq. (19) for singular operators—e.g., those expressible through Dirac distributions. For such operators Ψ_1, defined by Eq. (21), or Φ_1, defined by Eq. (22), are not ordinary functions and cannot be computed using the conventional approximation techniques valid for functions belonging to a suitable Hilbert space. Nevertheless, if we formally solve Eqs. (21) and (22) by minimizing the corresponding Hylleraas functionals

$$J[\tilde{\Psi}] = \langle\tilde{\Psi}|h - e|\tilde{\Psi}\rangle - 2\,\mathrm{Re}\langle\tilde{\Psi}|\mathcal{E}_1 - W|\psi\rangle, \tag{A1}$$

$$J[\tilde{\Phi}] = \langle\tilde{\Phi}|h_0 - e_0|\tilde{\Phi}\rangle - 2\,\mathrm{Re}\langle\tilde{\Phi}|\mathcal{E}_0 - W_0|\psi\rangle, \tag{A2}$$

with square-integrable trial functions $\tilde{\Psi}$ and $\tilde{\Phi}$, and subsequently insert the resulting "approximations" for Ψ_1 and Φ_1 into Eq. (19), then we obtain the correct answer for ΔW in the limit of an infinite basis set. Specifically, if the basis set χ_i, $i=1,\ldots,\infty$, employed to expand $\tilde{\Psi}$ is complete, the last term in Eq. (19) will be obtained as the $K\to\infty$ limit of the sequence

$$S_K = \langle\phi|v - e_1|\tilde{\Psi}_K\rangle, \tag{A3}$$

where

$$\tilde{\Psi}_K = \sum_{i=1}^{K} c_i\chi_i, \tag{A4}$$

and the coefficients c_i are determined from the set of K linear equations

$$\langle\chi_i|h - e|\tilde{\Psi}_K\rangle = \langle\chi_i|\mathcal{E}_1 - W|\psi\rangle, \tag{A5}$$

$i=1,\ldots,K$, resulting from the minimization of the functional (A1) with the trial function (A4). We assume here that the square-integrable basis functions χ_i are fixed—i.e., that the nonlinear parameters defining them are not reoptimized during the calculations. When W is a distribution, the functional (A1) is not bounded from below and the sequence $\tilde{\Psi}_K$ is not convergent. One can say that the sequence S_K is obtained from the variational collapse procedure controlled somehow by the fact that the nonlinear parameters are not optimized.

To prove that the procedure described above converges to ΔW, we have to make the rhs of Eq. (19) mathematically meaningful also when W is a distribution and Ψ_1 or Φ_1 are not well defined. We can do that by appropriate regularization of W. This means that the matrix elements $\langle f|W|g\rangle$ are interpreted as $n\to\infty$ limits of $\langle f|W^{(n)}|g\rangle$, where $W^{(n)}$ is a sequence of well-defined Hilbert space operators. It is well known that the sequence $\delta^{(n)}(\mathbf{r})=(n/\pi)^{3/2}e^{-nr^2}$ regularizes the Dirac distribution. For the p^4 operator we can use the sequence of operators $(p^4)^{(n)}=np^4/(n+p^4)$, defined in the momentum space and Fourier transformed back to the position space. The operators $\delta^{(n)}(\mathbf{r})$ and $(p^4)^{(n)}$ are bounded, so the derivations of Sec. II become legitimate if W is replaced by the operator $W^{(n)}$ constructed from these operators. ΔW is then well defined by computing the rhs of Eq. (19) with W replaced by $W^{(n)}$ and taking the limit $n\to\infty$ at the very end. Specifically the last term in Eq. (19) is defined as the $n\to\infty$ limit of the sequence of matrix elements $\langle\phi|v-e_1|\Psi_1^{(n)}\rangle$, where $\Psi_1^{(n)}$ is a solution of Eq. (21) in which W is replaced by $W^{(n)}$.

To show that $\langle\phi|v-e_1|\Psi_1\rangle$ defined by this regularization procedure can be obtained as the $K\to\infty$ limit of the S_K approximants of Eq. (A3), we introduce an auxiliary function ψ_1 satisfying the equation

$$(h-e)\psi_1 = (e_1 - v)\phi \tag{A6}$$

and the normalization condition $\langle\psi_1|\psi\rangle=0$. Using Eq. (A6) and subsequently Eq. (21) with W replaced by $W_1^{(n)}$, we can write

$$\langle\phi|v-e_1|\Psi_1^{(n)}\rangle = -\langle\psi_1|h-e|\Psi_1^{(n)}\rangle = \langle\psi_1|W_1^{(n)} - \mathcal{E}_1^{(n)}|\psi\rangle, \tag{A7}$$

where $\mathcal{E}_1^{(n)}=\langle\psi|W_1^{(n)}|\psi\rangle$. Taking the $n\to\infty$ limit of the extreme sides of Eq. (A7), we find

$$\langle\phi|v-e_1|\Psi_1\rangle = \langle\psi_1|W_1 - \mathcal{E}_1|\psi\rangle, \tag{A8}$$

where the rhs of Eq. (A8) can now be computed directly without regularization [i.e., using the usual definition $\langle\phi|\delta(\mathbf{r})|\psi\rangle=\phi^*(0)\psi(0)$ or $\langle\phi|p^4|\psi\rangle=\langle p^2\phi|p^2\psi\rangle$].

Equation (A6) is a linear inhomogeneous equation with a well-defined square-integrable function on the right-hand side and a positive-definite operator on the left-hand side. The solution of this equation can be obtained by the minimization of the Hylleraas functional of the form of Eq. (A1) with $(\mathcal{E}_1-W)\psi$ replaced by $(e_1-v)\phi$. Unlike the functional of Eq. (A1) the functional corresponding to Eq. (A6) is bounded from below and the sequence of approximants generated by the variational procedure converges to the exact solution ψ_1. If the basis set employed to expand ψ_1 is the same as that employed to compute the (divergent) sequence $\tilde{\Psi}_K$, the sequence of variational approximations to ψ_1 is given by

$$\tilde{\psi}_K = \sum_{i=1}^{K} d_i\chi_i, \tag{A9}$$

where the linear coefficients d_i are determined from the set of K linear equations

$$\langle\chi_i|h-e|\tilde{\psi}_K\rangle = \langle\chi_i|e_1-v|\phi\rangle, \tag{A10}$$

$i=1,\ldots,K$. Since $\tilde{\psi}_K$ converges to ψ_1 when $K\to\infty$, the series of matrix elements $T_K=\langle\tilde{\psi}_K|W_1-\mathcal{E}_1|\psi\rangle$ must converge to $\langle\psi_1|W_1-\mathcal{E}_1|\psi\rangle$ and, in view of Eq. (A8), to $\langle\phi|v-e_1|\Psi_1\rangle$.

To relate T_K and S_K we consider the matrix element $\langle\tilde{\psi}_K|h-e|\tilde{\Psi}_K\rangle$. In view of Eq. (A5) this matrix element is equal to $\langle\tilde{\psi}_K|\mathcal{E}_1-W_1|\psi\rangle=-T_K$. On the other hand, using Eq. (A10) we can represent $\langle\tilde{\psi}_K|h-e|\tilde{\Psi}_K\rangle$ as $\langle\phi|e_1-v|\tilde{\Psi}_K\rangle=-S_K$. Thus, $S_K=T_K$. This shows that the sequence of approximants S_K resulting from the divergent (collapsing) variational procedure based on the functional (A1) converges to $\langle\phi|v-e_1|\Psi_1\rangle$—i.e., to the “right result.” In the same way one can prove that the second term on the rhs of Eq. (19) can be computed by minimizing the functional of Eq. (A2). This completes the proof that Eq. (19), combined with a formal variational solution of Eqs. (21) and (22), gives the correct value of ΔW also when W is a distribution operator.

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