Long-range asymptotics of exchange energy in the hydrogen molecule

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The exchange energy, the splitting between gerade and ungerade states in the hydrogen molecule is investigated in the limit of a large internuclear distance. Accurate numerical calculations of the exchange energy have proven to be very difficult and there are conflicting analytic results in the literature concerning its asymptotics. To resolve this prevailing controversy, we employed an explicitly correlated exponential basis for highly accurate variational calculations of the exchange energy in H₂ up to internuclear distances of 57.5 Bohr radii and compared it to all the known analytic asymptotic expansions. Our numerical calculations support the leading term of the form \( R^{5/2} e^{-2R} \).

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I. INTRODUCTION

The hydrogen molecule, assuming clamped nuclei, is described by the electronic wave function, which can be symmetric or antisymmetric with respect to exchange of electrons and with respect to inversion through the geometrical center. For a large internuclear separation the symmetry of the wave function does not matter, and one has two separate hydrogen atoms. It means that the difference between symmetric and antisymmetric state energies has to be exponentially small. Indeed, this splitting behaves as \( e^{-2R} \), but the question remains concerning the prefactor. If we assume that the wave function is just a product of two properly symmetrized hydrogen orbitals, the so-called Heitler-London wave function [1], then the splitting is of the form given by Eq. (5), which is known to be invalid, even with regard to its sign [2]. It means that, even for large internuclear distances, one cannot assume that the electronic wave function is a symmetrized product of hydrogenic ones. Therefore, the interesting question is about a correct asymptotics of the exchange energy and the functional form of the wave function that reproduces this asymptotic behaviour.

Regarding analytic calculations of the exchange energy, there are conflicting results even for the leading term, and no results for subleading ones. Since we were not able to rigorously rederive this leading asymtotics by ourselves, we developed a numerical approach to resolve and verify the exchange energy at large internuclear distances. To achieve it, we employed a large basis of exponential functions of the generalized Heitler-London form with an arbitrary polynomial in all interparticle distances. We have previously developed an efficient recursive approach to calculate integrals with two-center exponential functions [3], and in this work use a parallel version of linear algebra in an arbitrary precision arithmetic to fully control the precision of the exchange energy. For example, we used about 230 digits arithmetic at the largest internuclear separations of 57.5 au to obtain three digits of the exchange energy out of 50 digits for the total energy. To our knowledge, there is no better approach that will give the exchange energy through perturbative treatment with full control of the numerical precision. In fact, the widely used Symmetry Adapted Perturbation Theory (SAPT) method [4], which aims to extract the exchange energy contribution in a perturbative manner, has pathologically slow convergence [5][6] for large internuclear distances, and its results are far from being accurate.

II. FORMULATION OF THE PROBLEM

Let us consider a stationary Schrödinger equation for two electrons with positions given by \( \vec{r}_1 \) and \( \vec{r}_2 \) in the H₂ molecule in the Born-Oppenheimer approximation with internuclear separation \( R \),

\[ H \Psi_g(\vec{r}_1, \vec{r}_2) = E_g(R) \Psi_g(\vec{r}_1, \vec{r}_2), \]

\[ H \Psi_u(\vec{r}_1, \vec{r}_2) = E_u(R) \Psi_u(\vec{r}_1, \vec{r}_2), \]

where subscripts \( g \) and \( u \) denote gerade and ungerade symmetry under the inversion with respect to the geometrical center. They correspond to the ground electronic states with a total spin \( S = 0 \) and \( S = 1 \). \( H \) in the above is the nonrelativistic Hamiltonian of the hydrogen molecule with clamped nuclei,

\[ H = -\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} - \frac{1}{r_{1A}} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} - \frac{1}{r_{2B}} + \frac{1}{r_{12}} + \frac{1}{R} \]

Within the Born-Oppenheimer approximation, one considers only the electronic part of the wave function of the system, and thus \( R \) serves as a parameter for electronic energies. The difference between these energies

\[ \Delta E = E_u - E_g \]

is the energy splitting, and half of this splitting with the minus sign, \( J = -\Delta E/2 \), was the exchange energy according to the definition used in previous works. In this work we always refer to \( \Delta E \) and convert results of the previous works from \( J \) to \( \Delta E \). Consequently, we use the exchange energy as a synonym of the energy splitting.

The pioneering theory of Heitler and London [1] was one of the first attempts to explain chemical bonding [7] on the grounds of freshly established foundations of quantum mechanics. Their method was based on approximation of the wave functions corresponding to the lowest energy states of H₂ with symmetrized and antisymmetrized products of the exact hydrogen atom solutions. This approach was pursued in
the same year by Sugiuira [8] who derived Born-Oppenheimer energies of lowest gerade and ungerade states as a function of $R$. The asymptotic value for the energy splitting based on Sugiuira [8] reads,

$$\Delta E_{HL}(R) = 2 \left[ \frac{28}{15} - \frac{2}{15} \ln R + \gamma_E \right] R^3 \exp(-2R) + \mathcal{O}\left(R^2 \exp(-2R)\right), \quad (5)$$

where $\gamma_E = 0.577 215...$ is the Euler-Mascheroni constant.

The Heitler-London approach appeared plausible because it provided a reasonable mechanism of chemical bond formation and its comparison with the results of ab-initio numerical calculations [9, 10] obtained later was satisfactory. Nevertheless, its long-range asymptotics is inherently flawed based on the physical grounds. Analysis of Eq. (5) reveals that the asymptotic behavior of $\Delta E$ in Heitler-London theory becomes unacceptable, due to the logarithmic term being dominant as $R \to \infty$. As a consequence, for sufficiently large $R$ ($\approx 60$ au) energy splitting becomes negative. The negative sign of $\Delta E_{HL}(R)$ contradicts the well-established theorem on Sturm-Liouville operators with homogeneous boundary conditions stating that the lowest energy eigenstate should be nodeless in the coordinate space.

Many years later, it was recognized that the Heitler-London approach underestimates electron correlations [2], and the logarithmic term in Eq. (5) could be identified with a potential coming from the exchange charge distribution. This line of reasoning lead to conjectures (see Refs. [11–13]), that the correct asymptotics might be in the same form as Heitler-London if only the logarithmic term is appropriately suppressed (e.g. via proper treatment of electron correlations).

Indeed, Burrows et al. [13] on the grounds of algebraic perturbation theory [14] have derived their formula for the long-range asymptotics of the splitting

$$\Delta E_{BDC}(R) = R^3 e^{-2R} \left( \gamma_{BDC} + \mathcal{O}\left(\frac{1}{R}\right)\right), \quad (6)$$

with $\gamma_{BDC} = 0.301 672...$, a result similar to the Heitler-London result given by Eq. (5) aside from the unphysical logarithmic term.

A completely different line of reasoning was introduced by Gor’kov and Pitaevskii [15], followed only a few months later with a very similar method by Herring and Flicker [16]. They both used a kind of quasiclassical approximation for the wave function to derive its asymptotic form, and with the help of a surface integral summarized by Eq. (2), they obtained the exchange energy. A mistake in the numerical coefficient of the leading term in the former was indicated and corrected in the latter paper [16], and their final result is

$$\Delta E_{HF} = \gamma R^{5/2} \exp(-2R) + \mathcal{O}\left( R^2 \exp(-2R) \right), \quad (7)$$

with the leading order coefficient

$$\gamma = 1.636 572 063... \quad (8)$$

Accounting for the asymptotic wave function requires careful analysis of various regions of the 6-dimensional space (see for instance Ref. [16]). With the increasing internuclear distance the exact wave function approaches a symmetrized or antisymmetrized product of two isolated hydrogen atom solutions. Nonetheless, the exact way in which this limit is approached is of paramount importance for the asymptotics of exchange energy, as has been thoroughly discussed with the case of Heitler-London theory in Ref. [2]. In comparison to analytic approaches for $H_2^+$ [17–20], examination of asymptotic energy splitting in $H_2$ is substantially more challenging problem due to electron-electron correlations, and it is prone to mistakes, as made evident by the presence of conflicting results in the literature [12 13 15 16], compare Eqs. (6) and (7).

III. DERIVATION OF THE LEADING ASYMPTOTICS

To our knowledge, all of the analytic derivations presented in Refs. [11–16, 21–22] ultimately rely on the Surface Integral Method (SIM), also referred to in the literature as the Smirnov [23] or Holstein-Herring [24] method. Here we follow the work of Gor’kov and Pitaevskii [15] to present SIM and the derivation of the asymptotic exchange energy in Eq. (7). This derivation lacks mathematical rigor, but nevertheless helped us to understand the crucial behavior of the asymptotic wave function. Moreover, their asymptotics is confirmed by our numerical calculations.

Let us assume that nuclei are on the $z$-axis with $z = a, -a$, $(R = 2a)$, and let $\Omega$ be a half of the 6-dimensional space with $z_2 \geq z_1$, and $\Sigma$ is a boundary of $\Omega$, namely 5-dimensional space with $z_1 = z_2$. Consider the following integral

$$\langle E_g - E_u \rangle \int_{\Omega} d^3r_1 d^3r_2 \Psi_g \Psi_u$$

$$= \frac{1}{2} \int_{\Omega} d^3r_1 d^3r_2 \left[ \Psi_g (\Delta_1 + \Delta_2) \Psi_u - \Psi_u (\Delta_1 + \Delta_2) \Psi_g \right]$$

$$= \int_{\Omega} d^3r_1 d^3r_2 \nabla_1 \left[ \Psi_g \nabla_1 \Psi_u - \Psi_u \nabla_1 \Psi_g \right]$$

$$= \int_{\Sigma} d^2s \left[ \Psi_g \nabla_1 \Psi_u - \Psi_u \nabla_1 \Psi_g \right]. \quad (9)$$

Let us introduce a combination of functions

$$\Psi_1 = \frac{1}{2}(\Psi_g + \Psi_u), \quad (10)$$

$$\Psi_2 = \frac{1}{2}(\Psi_g - \Psi_u), \quad (11)$$

with respective phase chosen in a manner that $\Psi_{1,2}$ are real and correspond to electron localized at a specific nucleus, namely

$$\Psi_1 \approx \frac{1}{\pi} e^{-|\vec{r}_1 + \vec{a}|-|\vec{r}_2 - \vec{a}|}, \quad \text{for } \vec{r}_1 \to -\vec{a}; \vec{r}_2 \to \vec{a} \quad (12)$$

$$\Psi_2 \approx \frac{1}{\pi} e^{-|\vec{r}_1 - \vec{a}|-|\vec{r}_2 + \vec{a}|}, \quad \text{for } \vec{r}_1 \to \vec{a}; \vec{r}_2 \to -\vec{a} \quad (13)$$

and $\Psi_{g/u}$ functions are normalized to 2. The left-hand side of
Eq. (9) can be transformed to
\[
\int_{\Omega} d^{3}r_{1} d^{3}r_{2} \Psi_{g} \Psi_{u} = \frac{1}{2} \int_{\Omega} d^{3}r_{1} d^{3}r_{2} \left[ \Psi_{g}^{2} + \Psi_{u}^{2} - (\Psi_{g} - \Psi_{u})^{2} \right]
\]
and the right hand side to
\[
\int_{\Sigma} d\vec{S} \left[ \Psi_{g} \nabla_{\Sigma} \Psi_{u} - \Psi_{u} \nabla_{\Sigma} \Psi_{g} \right] = 2 \int_{\Sigma} d\vec{S} \left[ \Psi_{2} \nabla_{\Sigma} \Psi_{1} - \Psi_{1} \nabla_{\Sigma} \Psi_{2} \right].
\]
As a result, one obtains
\[
E_{g} - E_{u} = \frac{2}{1 - 2} \int_{\Omega} dV \Psi_{1}^{2} = \frac{2}{1 - 2} \int_{\Omega} dV \Psi_{2}^{2}.
\]
(16)

The second term in the denominator is exponentially small, and thus can be safely neglected. By virtue of Eq. (16), the knowledge of the wave function and its derivative on \( \Sigma \) is sufficient to retrieve the energy splitting. The advantage of this method manifests itself especially in the regime of large internuclear distance, where exact wave functions of singlet and triplet states are close to the appropriately symmetrized and antisymmetrized products of the isolated hydrogen atom solutions.

Below we closely follow procedure of Ref. [15] and correct several misprints there. Let us assume the following ansatz of the wave functions \( \Psi_{1/2} \)
\[
\Psi_{1}(\vec{r}_{1}, \vec{r}_{2}) = \frac{\chi_{1}(\vec{r}_{1}, \vec{r}_{2})}{\sqrt{\pi}} e^{-|\vec{r}_{1} + \vec{a}| - |\vec{r}_{2} - \vec{a}|},
\]
(17)
\[
\Psi_{2}(\vec{r}_{1}, \vec{r}_{2}) = \frac{\chi_{2}(\vec{r}_{1}, \vec{r}_{2})}{\sqrt{\pi}} e^{-|\vec{r}_{1} - \vec{a}| - |\vec{r}_{2} + \vec{a}|},
\]
(18)
where the functions \( \chi_{1/2} \) change slowly in comparison to the exponential terms. One considers the region of \( z_{1} \approx a, z_{2} \approx -a \) and \( \rho_{1}, \rho_{2} \sim \sqrt{a} \) where the exponentials become
\[
e^{-|\vec{r}_{1} + \vec{a}| - |\vec{r}_{2} - \vec{a}|} \sim \exp \left\{ -2a - z_{1} + z_{2} - \frac{\rho_{1}^{2}}{2(a + z_{1})} - \frac{\rho_{2}^{2}}{2(a - z_{2})} \right\},
\]
(19)
and \( \rho_{i} \) is the perpendicular distance of \( i \)-th electron from the internuclear axis. From the Schrödinger equation one obtains for \( \chi_{1} \)
\[
\left[ \frac{\partial}{\partial z_{1}} - \frac{\partial}{\partial z_{2}} + \frac{1}{2a - a - z_{1}} - \frac{1}{a + z_{2}} + \frac{1}{|\vec{r}_{1} - \vec{r}_{2}|} \right] \chi_{1} = 0,
\]
(20)
where higher order \( O(1/\sqrt{a}) \) terms are neglected. Introducing \( z_{1} = (\xi + \eta)/2 \) and \( z_{2} = (\xi - \eta)/2 \), this equation takes the form
\[
\left[ \frac{\partial}{\partial \eta} - \frac{1}{2a - \xi - \eta} - \frac{1}{2a + \xi - \eta} + \frac{1}{2\sqrt{\eta^{2} + \rho_{12}^{2}}} + \frac{1}{4a} \right] \chi_{1} = 0,
\]
(21)
and the general solution is
\[
\chi_{1} = C(\xi, \rho_{12}) e^{-\frac{\eta}{\sqrt{2}} \frac{\sqrt{\eta^{2} + \rho_{12}^{2} - \eta}}{(2a - \xi - \eta)(2a + \xi - \eta)}},
\]
(22)
up to the unknown function \( C(\xi, \rho_{12}) \). This constant is determined from the condition that whenever \( \vec{r}_{1} \approx -\vec{a} \) or \( \vec{r}_{2} \approx \vec{a} \) the wave function \( \Psi_{1} \) should be just exponential, and thus \( \chi_{1} = 1 \) in this region. This argument can be justified, since for \( \vec{r}_{1} \approx -\vec{a} \), the second electron interacts dominantly with its nucleus. From this condition one obtains
\[
\Psi_{1}(\vec{r}_{1}, \vec{r}_{2}) = \frac{2a(2a - |z_{1} + z_{2}|)}{\pi(a + z_{1})(a + z_{2})} \exp \left( \frac{1}{2} - z_{1} + z_{2} - \frac{\rho_{1}^{2}}{2(a + z_{1})} - \frac{\rho_{2}^{2}}{2(a - z_{2})} \right) \times \sqrt{\frac{(z_{1} - z_{2})^{2} + \rho_{12}^{2} + z_{2} - z_{1}}{(2a - |z_{1} + z_{2}|)^{2} + \rho_{12}^{2} + 2a - |z_{1} + z_{2}|}} \exp \left( -\frac{1}{2} + \frac{z_{2} - z_{1} + |z_{1} + z_{2}|}{4a} \right).
\]
(23)

The function \( \Psi_{2} \) is obtained by a replacement \( \vec{r}_{1} \leftrightarrow \vec{r}_{2} \). The appearance of \( \rho_{12} \) in the wave functions \( \Psi_{1} \) is in crucial distinction to the Heitler-London wave function and ensures the correct sign of the leading order asymptotics for all distances, as pointed out in Ref. [25]. \( \Psi_{1} \), however, is not differentiable at \( z_{1} + z_{2} = 0 \) and this is one of the reasons we were not able to fully accept this derivation. A similar problem appears in a later derivation of Herring and Flicker [16] and this lack of analyticity at \( z_{1} + z_{2} = 0 \) was somehow ignored in all the previous works. One may even ask a question, why this nonanalytic wave function should give the right asymptotics and here we show that indeed, it is in agreement with our numerical calculations.

Let us now return to Eq. (16) to obtain the energy splitting
from the above Ψ. Since χ_{1/2} is slowly changing in comparison to dominant exponentials, their derivative can be neglected with that of exponentials, and the splitting becomes

\[ E_g - E_a = -8 \int_0^a dz d^2r_1 d^2r_2 \Psi_2 \Psi_1 \bigg|_{\ z_1=z_2=z}, \]  

(24)

where

\[ \Psi_2 \Psi_1 \bigg|_{\ z_1=z_2=z>0} = \frac{(2\alpha) \rho_{12} e^{-4a-1}}{\pi^2(a-z)^2} \frac{\ e^{\frac{1}{2} \frac{\alpha}{2} (\rho_1^2 + \rho_2^2)}}{\sqrt{\pi/2}}, \]

(25)

where only the leading terms in the limit of a large \( a \) are retained. Integrals over \( \rho_1, \rho_2 \) yield

\[ \int d^2r_1 d^2r_2 \rho_{12} e^{-\alpha (\rho_1^2 + \rho_2^2)} = \pi^2 \sqrt{\frac{\pi}{2}} \alpha^{-5/2}. \]

(26)

As a result one is left with the one-dimensional \( z \)-integral

\[ E_g - E_a = -32e^{-4a-1} \int z \ e^{z/a} (a-z)^{3/2} (a+z)^{1/2}, \]

(27)

which upon change of variable \( q = 1 - z/a \) yields

\[ E_g - E_a = -16 \sqrt{2\pi} a^{5/2} e^{-4a} \int q^{1/2} (2-q)^{1/2}. \]

(28)

After noting that \( a = R/2 \), this result

\[ \gamma = 4\sqrt{\pi} \int_0^1 dx e^{-x} x^{3/2} (2-x)^{1/2} \]

(29)

coincides with Eq. (19) of Ref. [16] and will be verified in the next Sections by direct numerical calculations.

### IV. VARIATIONAL APPROACH

In this approach one solves the Schrödinger equation by representing the wave function as a linear combination of some basis functions and finds linear coefficients from the variational principle. Since we are interested in the large \( R \) asymptotics of the exchange energy, the only viable option is to employ an exponential basis. This ensures the short-range cusp conditions [26] and correct long-range asymptotic behavior of the trial wave function. Consequently, the basis of trial functions is chosen in the following form

\[ \phi = \sum_{\{n_i\}} c_{\{n_i\}} (1 \pm P_{AB}) (1 \pm P_{12}) e^{-r_1 A - r_2 B} \]

(30)

\[ \times \eta_1^{n_1} \eta_2^{n_2} \xi_1^{n_3} \xi_2^{n_4} e^{n_5}, \]

where

\[ \eta_i = r_i A - r_i B, \ \xi_i = r_i A + r_i B, \]

(31)

and where \( P_{AB} \) and \( P_{12} \) represent operators enforcing symmetry with respect to the permutation \( r_1 A \leftrightarrow r_2 B \) and \( r_1 B \leftrightarrow r_2 A \). Only one type of exponent is used in the wave function, because the ionic structures like \( \text{H}^+ \text{H}^- \), which correspond to a different choice of the exponent \( e^{-r_1 A - r_1 B} \), are subdominant in our problem, as was already discussed in Ref. [2], and thus they can be omitted.

It is tempting to assume that the sum over non-negative integer indices \( n_i \) is chosen such that for the so-called shell number \( \Omega \)

\[ \sum_{i=1}^5 n_i \leq \Omega, \]

(32)

because it gives a good numerical convergence for the total binding energy. However, the main problem here is the very low numerical convergence of the exchange energy at large internuclear distances \( R \) with the increasing size of the basis as given by \( \Omega \). It was the main reason that previous numerical attempts were not very successful.

One notes that for \( R \to \infty \), the main contribution to the numerator of the surface integral in Eq. (20) comes from the integration over the neighborhood of the internuclear axis. We thus anticipate that the crucial behavior of the wave function is encoded in \( \eta_{1,2} \). Consequently, a basis is constructed using three independent shell parameters, such that the sum of powers of \( \eta_{1,2}, \xi_{1,2} \), and \( r_1 \) are controlled by corresponding shell numbers \( \Omega_A, \Omega_B, \) and \( \Omega_C \)

\[ n_2 + n_3 \leq \Omega_A, \ n_4 + n_5 \leq \Omega_B, \ n_1 \leq \Omega_C, \]

(33)

and numerical convergence is attained independently in each shell parameter.

Matrix elements of the nonrelativistic Hamiltonian can be expressed in terms of direct and exchange integrals of the form

\[ f_{n_0 n_1 n_2 n_3 n_4}(R) = R \int \frac{d^3r_1}{4\pi} \int \frac{d^3r_2}{4\pi} \frac{e^{-w_1 r_1 - w_2 r_2}}{r_1 A r_1 B r_2 A r_2 B} \times \sum_{\{n\}} c_{\{n\}} \left[ \eta_1^{n_1} \eta_2^{n_2} \xi_1^{n_3} \xi_2^{n_4} e^{n_5} \right], \]

(34)

with non-negative integers \( n_i \). When all \( n_i = 0 \) \( f \) is called the master integral, see Ref. [3]

\[ f(R) = R \int \frac{d^3r_1}{4\pi} \int \frac{d^3r_2}{4\pi} \frac{e^{-w_1 r_1 - w_2 r_2}}{r_1 A r_1 B r_2 A r_2 B} \times \sum_{\{n\}} c_{\{n\}} \left[ \eta_1^{n_1} \eta_2^{n_2} \xi_1^{n_3} \xi_2^{n_4} e^{n_5} \right]. \]

(35)

All integrals \( f_{n_0 n_1 n_2 n_3 n_4}(R) \) can be constructed through differentiation of the master integral with respect to the nonlinear parameters and can be reformulated into stable recurrence relations [3], providing a way to obtain all the integrals required to build matrix elements. Details on computation of necessary integrals and matrix elements can be found in our previous works in Refs. [3, 27, 28].

Having constructed the Hamiltonian and overlap matrices, the energy and linear coefficients \( c_{n_0 \ldots n_4} \) are determined by the secular equation,

\[ \det \left[ \langle n_0 \ldots n_4 | H | n_0' \ldots n_4' \rangle - E \langle n_0 \ldots n_4 | n_0' \ldots n_4' \rangle \right] = 0. \]

(36)
It has to be solved separately for \(E_g\) and \(E_u\). Consequently, to retrieve an exponentially small difference between eigenvalues for large internuclear distances, employment of extended-precision arithmetic is inevitable, and for this we chose to use the MPFR library [32].

The generalized eigenproblem in Eq. (35) is solved with the help of the Shifted Inverse Power Method. At each iteration the linear system has to be solved to refine the initial eigenvalue guess, which is done via calculation of the exact Cholesky factor of the \(H-E_S\) matrix, where \(H\) is the Hamiltonian and \(S\) the overlap matrix. A significant drawback of the applied basis is the fact that those matrices are dense, far from diagonally dominant and near-singular, especially for large \(R\). This specific structure of matrices in the explicitly correlated exponential basis gives no comfort of iterative (e.g. Krylov-like) methods. Computation of the exact inverse Cholesky factor proved to be a suitable approach, providing cubic convergence. A crucial advantage of this method is that the Cholesky factor has to be computed only once and can be reused in every iteration. The main drawback of performing full Cholesky factorization is its algorithmic complexity. It requires \(n^3/3\) arithmetic operations in arbitrary precision, which eventually become a bottleneck of the whole calculation. Total computation time can be significantly reduced when Cholesky factorization is parallelized. We have found our implementation of procedure HSL_MP54 for dense Cholesky factorization from the HSL library [30,31] adopted to arbitrary precision to perform best in terms of performance and accuracy.

Relying on our previous calculations of the Born-Oppenheimer potential for \(H_2\) [29] and anticipating that variational calculations will follow one of the analytic results for the leading asymptotics of energy splitting, \(\Delta E_{BCD}(R) \sim R^3e^{-2R}\) or \(\Delta E_{HF}(R) \sim R^{5/2}e^{-2R}\) with the coefficient of order of unity, the accuracy goal in decimal digits can be estimated as \([\log_{10}(\Delta E)] + n\). It is the number of correct digits in \(E_g\) and \(E_u\) required to obtain the difference between them on \(n\) last significant digits. In the extreme case of the internuclear distance \(R = 57.5\) au, approximately 50 correct digits in the final numerical value of \(E_g\) and \(E_u\) are required. Consequently, solving generalized eigenvalue problems for \(E_g\) and \(E_u\) renders incorporating arbitrary precision in our computational method inevitable. We have found the MPFR library [32] to be robust and provide the best performance among all the publicly available arbitrary-precision software.

V. NUMERICAL RESULTS

It is crucial to properly choose \(\Omega\) parameters of the basis, in order to obtain a sufficiently accurate exchange energy. If we assume \(\Omega_B = \Omega_C = 0\), i.e. we allow only for a nontrivial dependence in \(n_1\) and \(n_2\), the energy splitting has a very low numerical convergence in \(\Omega_A\), and thus this shell parameter has to be sufficiently large to saturate the splitting. At the largest considered nuclear distance of 57.5 au the saturation was achieved with \(\Omega_A\) as large as 145. This demonstrates why previous numerical attempts were not successful. In fact, the only correct results were obtained in a previous work by one of us (KP) in Ref. [29], but the calculation was performed there only for internuclear distances up to \(R = 20\) au.

In contrast, numerical convergence in \(\Omega_C\) is very fast. Namely a value as small as \(\Omega_C = 4\) was sufficient to achieve the claimed numerical precision. We performed numerical calculations with increasing values of \(\Omega_A\) and \(\Omega_C\) shell parameters, but with \(\Omega_B = 0\) up to \(R = 57.5\). The limiting factor happened to be an available computer memory of 2TB, which was exhausted by recursive derivation of integrals with extended precision arithmetic. Corresponding numerical results are presented in the second column of Table I.

Considering the numerical convergence in \(\Omega_B\) it is relatively slow, but the numerical significance of the basis functions with \(n_4 + n_5 > 0\) becomes exponentially small in the limit of large internuclear distance \(R\). Therefore, we calculate \(\delta = R^{-5/2}e^{2R}(\Delta E - \Delta E(\Omega_B = 0))\) using single shell parameter \(\Omega\) as in Eq. (32) for all values of internuclear distances up to \(R = 35\), which was the upper limit set by the available computer memory. The obtained \(\delta\) as a function of \(R\) is very well fitted to the exponential functions of the form \(\alpha e^{-\beta R}\) with \(\alpha = -0.0477(8)\) and \(\beta = 0.1025(9)\), and we use this fit to obtain extrapolated \(\delta\) for internuclear distances \(R > 35\) au, as shown in Table I. This demonstrates that the correct asymptotics of the exchange energy can be obtained using basis functions with \(n_4 + n_5 > 0\) only. Nevertheless, the influence of functions with \(n_4 + n_5 > 0\) is included in order to obtain a complete numerical result for the exchange energy at individual values of \(R\).

The final results for the splitting, presented in the last column of Table I, are obtained as a sum of \(\Delta E(\Omega_B = 0)\) and \(\delta\). In view of the limitations of the available computer memory and reasonable computation times, we were able to perform calculations for \(R\) up to 57.5 au. To illustrate the computational cost of calculations, at \(R = 57.5\) au, the largest internuclear distance presented, \(\Omega_A = 145\) was required for saturation, which amounts to solving a dense eigenproblem in approx. 230 decimal-digit precision with basis size \(N \sim 27500\).

VI. NUMERICAL FIT OF THE ASYMPTOTIC EXPANSION

A brief analysis of numerical results gathered in Table I and depicted in Fig. reveals that even after rescaling by a factor of \(R^{-5/2}e^{2R}\) numerical data is still distant from \(\gamma\) from Eqs. [29],[8]. Nevertheless, around \(R = 35\) au monotonicity changes and very slow convergence to constant \(\gamma\) can be observed. Curiously, in the aforementioned \(\Omega_B = \Omega_C = 0\) basis, the rescaled exchange splitting \(R^{-5/2}e^{2R}\Delta E\) quickly converges as a function of \(R\), to a constant value of \(\gamma_0 = 1.3835(2)\). Inclusion of higher powers of \(r_{12}\) brings this constant close to the \(\gamma\), but even for the largest distances included in the calculations, numerical points are still distant from the asymptotic constant, as presented in Fig [I]. This is further evidence that the asymptotics is of the form \(R^{-5/2}e^{-2R}\), and even in a basis with no powers of \(r_{12}\), leading asymptotic behavior could be achieved, although with the coefficient \(\gamma_0\) smaller by \(\sim 20\%\).
TABLE I: Dependence of energy splitting $\Delta E = E_u - E_g$ scaled by a factor $R^{-5/2}e^{2R}$ on shell parameters at different internuclear distances $R$ [a.u.]. The first column presents $\Delta E$ as obtained with $\Omega_B = 0, \Omega_C = 0$, i.e. with no explicit correlation in the basis. The second is $\Delta$, the difference in energy splitting between $\Omega_B = \Omega_C = 0$ basis, and $\Omega_C \neq 0$ basis, and the third column is its value as extrapolated in $\Omega_C$, still with $\Omega_B$ fixed at zero. The fourth column shows a correction $\delta$ to $\Delta E$ due to $\Omega_B \neq 0$, and the last column is the total energy splitting. Uncertainty of $\Delta E(\Omega_B = 0, \Omega_C = 0)$, $\Delta$ and $\delta$ come from extrapolation in $\Omega_A, \Omega_B$, and $\Omega_B$, respectively.

| $R$   | $\Delta E(\Omega_B = 0, \Omega_C = 0)$ | $\Delta$ | $\Delta E(\Omega_B = 0)$ | $\delta$ | $\Delta E$ |
|-------|--------------------------------------|---------|--------------------------|---------|-----------|
| 20.0  | 1.418 595 21(9)                      | 0.138   | 1.557 565 0(18)          | -0.006 16(27) | 1.551 41(27) |
| 22.5  | 1.409 067 90(8)                      | 0.140   | 1.549 82 24(20)          | -0.004 76(22) | 1.545 06(22) |
| 25.0  | 1.402 295 96(8)                      | 0.142   | 1.549 444 3(22)          | -0.003 69(18) | 1.541 25(18) |
| 27.5  | 1.397 382 94(7)                      | 0.144   | 1.541 947 2(24)          | -0.002 86(15) | 1.539 09(15) |
| 30.0  | 1.393 761 45(5)                      | 0.146   | 1.540 212 6(26)          | -0.002 21(12) | 1.538 00(12) |
| 32.5  | 1.391 067 28(5)                      | 0.148   | 1.539 357 7(28)          | -0.001 71(97) | 1.537 64(97) |
| 35.0  | 1.389 047 31(5)                      | 0.150   | 1.539 116 6(30)          | -0.001 32(79) | 1.537 79(79) |
| 37.5  | 1.387 530 09(5)                      | 0.151   | 1.539 310 2(32)          | -0.001 02(5)  | 1.538 25(64) |
| 40.0  | 1.386 391 69(5)                      | 0.153   | 1.539 814 0(34)          | -0.000 79(4)  | 1.539 02(51) |
| 42.5  | 1.385 542 54(5)                      | 0.154   | 1.540 538 2(35)          | -0.000 61(4)  | 1.540 92(41) |
| 45.0  | 1.384 916 73(4)                      | 0.156   | 1.541 420 4(37)          | -0.000 47(3)  | 1.540 95(33) |
| 47.5  | 1.384 464 91(3)                      | 0.157   | 1.542 412 3(39)          | -0.000 36(8)  | 1.542 04(27) |
| 50.0  | 1.384 149 48(3)                      | 0.159   | 1.543 820 4(41)          | -0.000 28(21)| 1.543 97(21) |
| 52.5  | 1.383 941 70(2)                      | 0.160   | 1.544 602 6(44)          | -0.000 22(17)| 1.543 82(18) |
| 55.0  | 1.383 819 27(2)                      | 0.161   | 1.545 750 9(45)          | -0.000 17(14)| 1.545 58(15) |
| 57.5  | 1.383 764 60(2)                      | 0.163   | 1.546 874 3(41)          | -0.000 13(11)| 1.546 74(33) |

In order to perform a numerical fit, an important conclusion of the Herring- Flicker work [16] should be recalled, i.e. that the next asymptotic term should be of the relative order $1/\sqrt{R}$, but not $1/R$. This indicates that the general asymptotic series should be given in powers of $1/\sqrt{R}$. Slow convergence in the considered region of internuclear distances enforces accounting for at least 2 or 3 terms of asymptotic series to properly model the observed dependence. Taking into account subtleties concerning the number of points used for fitting and the number of terms in the asymptotic series, we can estimate the leading coefficient to be $1.657(26)$, in agreement with the Herring-Flicker value in Eq. (8). Moreover, a coefficient of $-0.66(7)$ for the next-to-leading $R^{-2}e^{2R}$ term is estimated by assuming the Herring-Flicker value for $\gamma$ and subsequent fitting in powers of $1/\sqrt{R}$. This value is in disagreement with the work of Andreev [22], where the next non-vanishing term is claimed to be $R^{3/2}e^{-2R}$.

![FIG. 1: Rescaled energy splitting $R^{-5/2}e^{2R}\Delta E$ fitted to numerical points in Table I in the range $R = 20 - 57.5$ au, Herring and Flicker [16] asymptotics is the red horizontal dashed line. Results for $R \leq 6, 20$ au are presented from Ref. [29] for completeness but were not used for fitting.](image1)

![FIG. 2: Rescaled energy splitting $R^{-3}e^{2R}\Delta E$ fitted in powers of $1/R$ to (rescaled) numerical points in Table I in the range $R = 20 - 57.5$ au. The Burrows-Dalgarno-Cohen [13] asymptotics is the red horizontal dashed line. Results for $R \leq 6, 20$ au are presented from Ref. [29] for completeness, but were not used for fitting. The leading coefficient being very close to zero indicates absence of the leading $R^{3}e^{-2R}$ term in the actual large-distance asymptotic expansion of exchange energy.](image2)
sumed, as in Fig. 2, its coefficient is very close to zero, indicating its absence in the asymptotic expansion at $R \to \infty$, in disagreement with the work of Burrows et al. \cite{13}. It is further evidence, that the leading asymptotics is $R^{3/2}e^{-2R}$, as obtained in Refs. \cite{15,16}.

VII. CONCLUSIONS

Our numerical results seem to resolve the controversy of the long-range asymptotics of the exchange energy in the hydrogen molecule. High numerical accuracy is achieved, owing not only to the correct asymptotic behavior of explicitly correlated exponential functions, but also due to the specific choice of the basis functions hinted by the significance of the internuclear axis neighborhood.

As conjectured by Hirschfelder and Meath \cite{33}, the $R^2e^{-2R}$ term is of significant magnitude in comparison to the leading order $R^{3/2}e^{-2R}$ term even for internuclear separations as large as $R = 50$ au. This is in strong disagreement with the derivation by Andreev \cite{22}, in which the coefficient of $R^2e^{-2R}$ is exactly zero. Our results are also in disagreement with the work of Burrows et al. \cite{13} in which the leading asymptotics of the energy splitting is $R^3e^{-2R}$ with a coefficient significantly different from 0.

To conclude, our numerical results revise the recent analytic derivations of the large-distance asymptotics and provide valuable benchmark for perturbative approaches.

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