

Excited Σ states of the hydrogen-antihydrogen molecule

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Adopting explicitly correlated Kołos-Wolniewicz-type basis functions, the Born-Oppenheimer potential curves of a number of excited Σ states of the hydrogen-antihydrogen system ($H\bar{H}$) were calculated for both, even and odd, Q symmetries, including also free positronium states. It is demonstrated that the excited leptonic states support rovibrational states with energies close to the ground-state dissociation threshold. As a consequence, the excited leptonic states need to be considered in theoretical treatments of ground-state $H-\bar{H}$ collisions.

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I. INTRODUCTION

Antimatter is not only fascinating by itself, but the evident asymmetry of matter and antimatter in our universe (together with the absence of a corresponding large amount of cosmic background radiation that would be expected from the annihilation of matter and antimatter when generated in equal amounts at the big bang) motivates experiments generating and trapping the simplest neutral compound antimatter atom, antihydrogen ($\bar{H}$) [1–5]. These experiments investigate possible violations of the charge-parity-time (CPT) conservation or the weak-equivalence principle (WEP) by comparing the spectroscopic properties or gravitational behavior of $\bar{H}$ with the ones of H , see, e. g., Refs. [6–10] and references therein.

With the experimental accessibility of the $\bar{H}$ atom, there is, on the other hand, also an increasing interest in its interaction with ordinary matter. In fact, long before the first experimental realization of antihydrogen atoms, the interaction with its matter counterpart, the hydrogen atom, was studied very carefully theoretically [11]. It was found that the Born-Oppenheimer Hamiltonian shows a symmetry closely related to charge-parity symmetry, called Q symmetry, which splits the eigenvalue spectrum into even and odd states. Using explicitly correlated basis functions in prolate spheroidal coordinates, known as Kołos-Wolniewicz basis functions, a very accurate ground-state potential curve was found, proving the local maximum found in Ref. [12] to be an artifact of the limited accuracy of the therein adopted numerical approach. Similar to the corresponding anion (cation) that is obtained, if one positron (electron) is removed from the $H\bar{H}$ system, it was found that the $H\bar{H}$ molecule is stable only above a critical distance R_c (also known as Fermi-Teller radius, as it was first mentioned in Ref. [13] for the corresponding one-lepton ion). Below R_c the system breaks up into protonium ($p\bar{p}$) and positronium ($e\bar{e}$), since the energy of $p\bar{p}$ and $e\bar{e}$ lies below

the one of $H\bar{H}$, at least within the Born-Oppenheimer approximation. The occurrence of a critical distance is intuitively understandable, as at some point the dipole formed by the proton and the antiproton is insufficient to bind the positronium (in the united-atom limit the positronium is evidently completely unbound). (A more stringent mathematical argument is given in Ref. [14].) However, the rather sharp change of the slope of the leptonic energy curve close to the critical distance led to some speculation. It may be caused by an avoided crossing between the molecular state and the one describing a free protonium-positronium pair, or the molecular state simply transforms continuously into the unbound state [15,16].

Besides the importance of $H\bar{H}$ as a paradigmatic matter-antimatter system, the interest in this system was also raised by a proposal to use ultracold H atoms for the sympathetic cooling of $\bar{H}$ [17] and the corresponding experimental progress in cooling H atoms, even achieving a Bose-Einstein condensate [18]. This initiated theoretical investigations regarding the question of whether the elastic cross section responsible for cooling can successfully compete with the destructive inelastic collisions, including the rearrangement into protonium and positronium and, of course, leptonic or hadronic annihilation [19–30] (see Ref. [31] for a short review), but also, e.g., a study investigating radiative association [32].

Most of those scattering calculations were based on the Born-Oppenheimer potential curve (possibly including adiabatic corrections) describing the interaction of H and $\bar{H}$, each being in their respective ground states [33]. This raised the question of how to treat the system for interhadronic separations $R < R_c$. In fact, it was shown by Strasburger, using explicitly correlated Gaussians, that the adiabatic correction terms diverge, if R approaches the critical distance R_c from above [34]. This hints at a complete breakdown of the Born-Oppenheimer approximation if the singularity should not turn out to be removable.

Most problematic is thus the treatment of the rearrangement channel into protonium and positronium with the question of a proper theoretical framework for $R < R_c$. In fact, since the protonium (and in principle also the positronium) can be left in different bound states, various rearrangement

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channels are accessible. Furthermore, the two particles (protonium and positronium) may have variable translational energy. The results obtained within the plane-wave [35] or distorted-wave [25] approximations were thus found to be improved, if the rearrangement channels were explicitly included using the Kohn variational method [23] or an optical potential [26]. In yet another approach, a mass-scaled Born-Oppenheimer potential was used to cope with the divergence close to the critical distance within a Born-Oppenheimer framework [36]. In view of the obtained results, in Ref. [16] the importance of the explicit inclusion of the rearrangement channels, e.g., in a close-coupling-type approach (see Eq. (7) in Ref. [16]) was emphasized. A general formulation of the required T matrix elements, including the approximation to include only a single molecular Born-Oppenheimer potential, is given in Ref. [37]. In Ref. [38] an approximation was formulated and adopted that requires the channels only in the asymptotic regime, i.e., for $R > R_c$, by invoking unitarity arguments. A natural, but computationally very demanding, extension is to directly treat the full four-body problem, as was done in Refs. [39–42]. Even if a very powerful four-body code, in this case one based on the Gaussian expansion method using different sets of Jacobian coordinates, exists [43], the calculation is extremely challenging, since the collision channel of hydrogen and antihydrogen involves very highly excited states, even if both atoms start in their ground state. The reason is that within a full four-body treatment, all the above-mentioned protonium and positronium channels are automatically included, starting with their ground states. The protonium ground-state energy is (within the nonrelativistic approximation) $E_{p\bar{p}} = -m_p/4 \approx -459.038$ a.u., but the dissociation energy of $H\bar{H}$ is within the same approximation -1.0 a.u.. (Atomic units Hartree are used throughout this work.) Using the complex-scaling method, scattering resonances close to the dissociation threshold were found that in an adiabatic picture would be associated to the protonium states with principal quantum numbers as high as 22 and 24 [41,42].

Despite the mentioned numerous studies of collisions between H and $\bar{H}$ or studies of the $H\bar{H}$ quasimolecule in Refs. [44,45], to the authors' knowledge all adiabatic calculations considered only the leptonic ground state of $H\bar{H}$ and its coupling to the protonium-positronium rearrangement channel. In fact, only in Refs. [46,47] Born-Oppenheimer potential curves for excited states appear to have been reported at all, but only for four non- Σ (Q -even) states. On the other hand, the present work investigates the excited $H\bar{H}$ states of Σ symmetry, considering both even and odd Q symmetries. Because, unlike for ordinary matter system like H_2 , the interaction between antiproton and proton is attractive, for small interhadronic separations this Coulombic attraction dominates the Born-Oppenheimer potentials of all leptonic states. Consequently, even in the limit of zero collision energy those excited states are energetically accessible to an antihydrogen atom scattering on a hydrogen atom, both being in their ground states. This allows for resonances to occur in which the incident atoms become energetically degenerate with some leptonically excited rovibrational molecular bound state. It is shown that despite the uncertainty of the proper treatment of the system below the critical distance within the Born-Oppenheimer

approximation adopted here, there is a plethora of rovibrational states that can lead to scattering resonances close to the ground-state dissociation limit of approximately -1.0 a.u.. Noteworthy, even if the kinetic energy of the colliding atoms would not perfectly agree with the excited molecular bound states, the resonance condition may be fulfilled, since also those bound states have a finite lifetime and thus a nonvanishing energy width due to annihilation and decay into protonium and positronium. Therefore, refined scattering calculations including the excited $H\bar{H}$ states need to be performed if reliable cross sections should be obtained. This conclusion is further supported by the findings of the full four-body calculations in Refs. [41,42] in which a resonance with dominant contribution from an excited positronium state ($n = 2$) appears to be relevant. As an interesting side aspect, it is demonstrated in the present work that (discretized) free-positronium states can be obtained also when using Kołos-Wolniewicz-type basis functions, if a basis set with two sets of noninteger exponents is used. This opens the way to corresponding close-coupling scattering calculations in which the rearrangement channels are intrinsically included. This avoids the use of two types of basis functions, one describing the molecular leptonic states and one the (free) positronium, that are computationally very demanding.

II. $H\bar{H}$ AND Q SYMMETRY

The $H\bar{H}$ system consists of a hydrogen and antihydrogen atom and is therefore the simplest neutral matter-antimatter molecule that can be studied. Its leptonic Hamiltonian is given by

$$\hat{H} = -\frac{1}{2}\nabla_e^2 - \frac{1}{2}\nabla_{\bar{e}}^2 - \frac{1}{r_{pe}} - \frac{1}{r_{\bar{p}\bar{e}}} - \frac{1}{r_{e\bar{e}}} + \frac{1}{r_{p\bar{e}}} + \frac{1}{r_{\bar{p}e}}, \quad (1)$$

where r_{ab} denotes the distance between constituents and p and e denote the proton and electron, respectively, while $\bar{p}$ and $\bar{e}$ denote their antimatter counterparts. Evidently, the Hamiltonian of $H\bar{H}$ differs from its corresponding matter counterpart H_2 only by an exchange of signs.

In Ref. [11] Kołos *et al.* introduced the $\hat{Q}$ symmetry operator, a composition of mirroring the leptons on a plane bisecting the interhadronic axis ($\hat{\sigma}_{lep}$) and permuting the leptons ($\hat{P}_{e\bar{e}}$). Both operations alone do not commute with the leptonic Hamiltonian,

$$\hat{\sigma}_{lep}\hat{H} = -\frac{1}{2}\nabla_e^2 - \frac{1}{2}\nabla_{\bar{e}}^2 - \frac{1}{r_{\bar{p}e}} - \frac{1}{r_{p\bar{e}}} - \frac{1}{r_{e\bar{e}}} + \frac{1}{r_{\bar{p}\bar{e}}} + \frac{1}{r_{pe}} \quad (2)$$

and

$$\hat{P}_{e\bar{e}}\hat{H} = -\frac{1}{2}\nabla_{\bar{e}}^2 - \frac{1}{2}\nabla_e^2 - \frac{1}{r_{p\bar{e}}} - \frac{1}{r_{\bar{p}e}} - \frac{1}{r_{e\bar{e}}} + \frac{1}{r_{pe}} + \frac{1}{r_{\bar{p}\bar{e}}}, \quad (3)$$

but leave the kinetic and $1/r_{e\bar{e}}$ terms unchanged while flipping the sign of all remaining terms. The Hamiltonian therefore is unchanged under the Q symmetry operation. This symmetry is not observed in ordinary matter molecules and is closely related to charge-parity (CP) symmetry. However, the leptonic Hamiltonian of $H\bar{H}$ possesses the same cylindrical symmetry around the interhadronic axis as any matter diatomic molecule. Therefore, the total angular momentum of

the electrons Λ is a good quantum number and one can solve for the Σ , Π , Δ , ... states separately. On the other hand, as all four particles are different, there is evidently no exchange symmetry and thus no ortho and para $\text{H}\bar{\text{H}}$, in contrast to the case of H_2 .

As was pointed out in Ref. [11], an advantage of the Q symmetry is that it is very suitable for calculations within the Born-Oppenheimer approximation, since within this approximation the Hilbert space of $\text{H}\bar{\text{H}}$ can be separated into Q -even and Q -odd leptonic wave functions. Thus, symmetry-adapted basis functions may be used to reduce the computational efforts. Furthermore, as long as the adiabatic approximation is a good approximation, selection rules with respect to leptonic transitions may be formulated. These may, of course, be completely different from the ones known for ordinary matter. For example, even the ground state with Σ symmetry (Q even) possesses a nonvanishing dipole moment allowing, e.g., for radiative transitions in between rovibrational states belonging to the same leptonic state [32].

III. NUMERICAL APPROACH

Despite being the simplest neutral matter-antimatter molecule, $\text{H}\bar{\text{H}}$ is still a four-body problem. Exact solutions are therefore difficult to obtain, especially for (highly) excited states. Therefore, the Born-Oppenheimer approximation is employed in which the wave function

$$\Psi_{m,v,J}(\mathbf{r}_p, \mathbf{r}_{\bar{p}}, \mathbf{r}_e, \mathbf{r}_{\bar{e}}) = \chi_{v,J,m_J}^{(m)}(\mathbf{R}) \psi_m(\mathbf{r}_e, \mathbf{r}_{\bar{e}}; R) \quad (4)$$

is assumed to be a single-product wave function of the hadronic (rovibrational) wave function $\chi_{v,J,m_J}^{(m)}$ that depends solely on the interhadronic separation vector $\mathbf{R} = \mathbf{r}_p - \mathbf{r}_{\bar{p}}$ and the leptonic wave function ψ_m that depends on the leptonic coordinates, but only parametrically on $R = |\mathbf{R}|$.

A. Leptonic problem

The leptonic wave functions and corresponding Born-Oppenheimer potential curves are obtained with the help of the computer program H2SOLV published by Pachucki *et al.* [48]. The code, written for diatomic two-electron molecules, was correspondingly modified for treating $\text{H}\bar{\text{H}}$, similar to the modification of the Kołos-Wolniewicz code in Ref. [20]. In more detail, for the Σ states considered here, the leptonic wave function ψ_m is expressed as a superposition

$$\psi_m(\mathbf{r}_e, \mathbf{r}_{\bar{e}}; R) = \sum_{\mathbf{n}} c_{m,\mathbf{n}}(R) \tilde{\phi}_{\mathbf{n}}(\mathbf{r}_e, \mathbf{r}_{\bar{e}}; R) \quad (5)$$

of so-called Kołos-Wolniewicz basis functions

$$\tilde{\phi}_{\mathbf{n}} = \exp(R(-y\eta_e - x\eta_{\bar{e}} - u\xi_e - w\xi_{\bar{e}})) \times r_{e\bar{e}}^{n_0} \eta_e^{n_1} \eta_{\bar{e}}^{n_2} \xi_e^{n_3} \xi_{\bar{e}}^{n_4} r^{1-n_0-n_1-n_2-n_3-n_4}, \quad (6)$$

where $\xi_j = (r_{p,j} + r_{\bar{p},j})/R$ and $\eta_j = (r_{p,j} - r_{\bar{p},j})/R$ are the prolate-spheroidal coordinates of lepton j (φ_j being its angle around the interhadronic axis). The index vector $\mathbf{n}$ contains the set of five integers (quintuple) $\{n_0, n_1, n_2, n_3, n_4\}$ that defines an individual Kołos-Wolniewicz *basis function*. A *basis set* is then characterized by the set of exponential parameters y, x, u , and w that is identical for all basis functions, being

henceforth called the *base* [49], and a selection of a set of quintuples $\mathbf{n}$.

Due to the very limited computational resources, Kołos and Wolniewicz selected in their original works on H_2 (and later for $\text{H}\bar{\text{H}}$) the quintuples $\mathbf{n}$ by hand. This selection, though extremely successful in obtaining very accurate results with astonishingly small basis sets, was hampered by linear dependencies between the basis functions due to the finite numerical precision. In H2SOLV this problem is overcome by adopting fortran libraries allowing for variable precision [50]. In this way, systematic convergence investigations for a given base can be performed by a systematic increase of the number of basis functions. In H2SOLV the integer parameter Ω is introduced for a complete characterization of a basis set, as all quintuples $\mathbf{n}$ that fulfill

$$\sum_{i=0}^4 n_i \leq \Omega \quad (7)$$

form a given basis set. A comparison of the results obtained for increasing values of Ω and calculating the relative difference to the result obtained with the largest value of Ω allows for a systematic convergence test. (Further refinement is possible by introducing upper limits for subsets of the n_j , e.g., separate upper limits for n_0 , $n_1 + n_2$, and $n_3 + n_4$.)

Insertion of the ansatz (5) for ψ into the leptonic Schrödinger equation leads to a generalized eigenvalue problem, since the basis functions are nonorthogonal. The solution of this eigenvalue problem yields the eigenvector $\mathbf{c}_m(R)$ and the leptonic energies $E_{\text{lep},m}(R)$. As in the case of ordinary molecules, the addition of the interhadronic attraction term, a simple constant, to the leptonic energy $E_{\text{lep},m}(R)$ yields the Born-Oppenheimer potential curve $V_m(R)$ for the leptonic state m .

Since the leptonic Hamiltonian in (1) obeys the Q symmetry as discussed above, the leptonic energy spectrum splits into states that are either even or odd with respect to Q symmetry. The introduction of the symmetry-adapted linear combination of Kołos-Wolniewicz basis functions

$$\phi_{\mathbf{n}}^{\pm} = \tilde{\phi}_{\mathbf{n}} \pm (-1)^{n_1+n_2} \tilde{\phi}_{\mathbf{n}}, \quad (8)$$

which are Q even or Q odd, respectively, leads to a substantial reduction of the computational time and memory needs. Especially, if many or even all eigenstates for a given basis set are requested, this effect is highly relevant, since the number of matrix elements that need to be calculated and the dimension of the matrix that needs to be diagonalized is reduced by about a factor of 2. Remember that variable precision needs to be adopted in order to cope with numerically caused linear dependencies, and this problem becomes more severe for larger basis sets (increasing values of Ω). Besides the linear dependencies that are due to finite numerical precision, additional true linear dependencies occur, if all symmetry-adapted basis functions obtained according to Eqs. (7) and (8) are included in the calculation, as this may lead even to zero-valued wave functions due to possible symmetries in the base parameters (y, x, u, w). These wave functions must thus be identified and filtered out in advance, as is described in detail in Appendix A.

While the Kołos-Wolniewicz basis functions in the limit $\Omega \rightarrow \infty$ form a complete basis (at least, if the practical

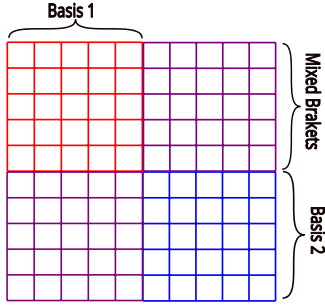


FIG. 1. Structure of the Hamiltonian matrix for a dual-base basis set, i.e., a basis set comprising two basis sets $\{\phi^{(0)}\}$ and $\{\phi^{(1)}\}$ with the different sets of exponential parameters (y_0, x_0, u_0, w_0) and (y_1, x_1, u_1, w_1) , respectively. This leads to three types of matrix elements: $\langle \phi_i^{(0)} | \hat{H} | \phi_j^{(0)} \rangle = \langle \phi_j^{(0)} | \hat{H} | \phi_i^{(0)} \rangle$ (red), $\langle \phi_i^{(1)} | \hat{H} | \phi_j^{(1)} \rangle = \langle \phi_j^{(1)} | \hat{H} | \phi_i^{(1)} \rangle$ (blue), and $\langle \phi_i^{(0)} | \hat{H} | \phi_j^{(1)} \rangle \neq \langle \phi_i^{(1)} | \hat{H} | \phi_j^{(0)} \rangle$ (purple).

problems of requiring possibly an infinite precision for reaching this hypothetical limit are ignored), the necessary sub-Hilbert space required for accurately describing a single or a number of states could be covered with much less basis functions, if different bases would be adopted. However, the historical success of the Kołos-Wolniewicz basis functions is due to the fact that using a single base allows for the very efficient evaluation of the Hamiltonian (and overlap) matrix elements, as they can be obtained via recursion from a master integral ($\mathbf{n} = \{0, 0, 0, 0, 0\}$). A natural compromise between a single base and, in the extreme case, one base per basis function is given by adopting a dual-, triple-, etc. base. In this way, also a possible continuous change of the character of a leptonic molecular state as a function of internuclear separation can be described efficiently. An example would be the admixture of an ionic component to a covalent state. Therefore, the extension to H2SOLV made here also includes the option to use multiple-base basis sets. Such an extension is rather straightforward, as is illustrated in Fig. 1 for the case of a dual base that is used in the present work. Since the product of two Kołos-Wolniewicz basis functions is again a Kołos-Wolniewicz basis function, only with different base parameters and quintuples, a dual base basically increases the number of master integrals roughly by a factor of 3. Of course, if the same Ω is used as for a single-base basis set, the dimension of the Hamiltonian matrix that needs to be diagonalized also increases by a factor of 2. The linear-dependency problem of Kołos-Wolniewicz basis functions caused by the finite numerical precision increases if a basis set with more than one base, but the same polynomial terms, is used. However, this problem was again solved by the variable precision arithmetics.

B. Optimization of the base parameters

Highly accurate calculations of leptonic states already of two-lepton systems such as H_2 or $\text{H}\bar{\text{H}}$ adopting finite basis sets require a careful individual optimization of all basis-set parameters for every single state. In the case of the lowest state of a given symmetry, the variational principle allows for a clear identification of the best basis set. Projecting out all energetically lower-lying states, the variational principle is

also strictly applicable to the excited states. If a set of states is obtained by diagonalization of the Hamiltonian matrix resulting from the linear ansatz (5), the enforced orthogonality is equivalent to projecting out the other states. Thus, the variational principle would be applicable to all states, but only if the representation of all lower-lying states would be exact. Although this is evidently not the case if a finite basis set is adopted like the one in this work, the variational principle is usually still reasonably well fulfilled, at least for the lower-lying excited states. Since the aim of this work is a reasonably good description of the lower-lying leptonic states, but not an extremely highly accurate description of individual states, a dual base with Ω values up to 10 was found to be a good compromise between required computational resources and achieved accuracy.

The choice of at least two bases, i.e., a dual-base basis set, was also motivated by the fact that from the previous results it is evident that the leptonic states of $\text{H}\bar{\text{H}}$ should comprise at least one molecular and one positronium component. Furthermore, the relative contribution of them should change with varying inter-hadronic separation. This information could have been used when optimizing the base parameters of the two bases. For example, one base could have been optimized by minimizing the $\text{H}\bar{\text{H}}$ ground-state energy, while the other base minimizes the energy of a free, more accurately “box” discretized positronium that would be obtained by setting both hadronic charges to zero [20,22]. However, since the present work aims primarily at a (reasonably) good description of a larger number of Born-Oppenheimer curves, a different strategy was pursued that, after numerous trials, was found to be more suitable for the present purpose.

The idea was that one base should provide a good description for large interhadronic distances where the atomic or molecular character should dominate, and one for small distances where the positronium character is expected to contribute, too. The most straightforward way would be to try to optimize all eight base parameters simultaneously, using as a criterion the energy minimization of a large number of states at different internuclear separations. However, this would not only pose a very challenging, if not (with the available computational resources) impossible, task but would also require to define a good minimization criterion. Evidently, for states with very different character it can easily occur that their energy ordering switches, depending on the base parameters. This effect is enhanced by the fact that with increasing energy the density of states also increases drastically. This leads to a very complicated, fine-structured optimization landscape with many local minima.

In order to avoid such complications, the parameters of the two bases (separately determined for both symmetries Q even and odd) were found independently, already reducing the number of parameters in each optimization from eight to four, leading to a dramatic reduction of the computational efforts. Furthermore, one base was solely optimized by minimizing the energy of the lowest-lying state (in the case of Q -even symmetry the ground state) at a single interhadronic separation ($R = 5.0 a_0$). A four-dimensional gradient descent algorithm was used to find the corresponding base parameters $\{y_0, x_0, u_0, w_0\}$. Since at large interhadronic separations as $R = 5.0 a_0$ the ground state is known to behave, in a very good

TABLE I. Optimized base parameters found by the procedure discussed in Sec. III B and used in the calculations of this work.

R	Symmetry	State	y	x	u	w
5.0	Q even	0	0.3	-0.5	0.5	0.5
0.8	Q even	2	-0.625	0.65	0.121 875	0.143 75
5.0	Q odd	0	-0.1	-0.5	0.3	0.5
0.8	Q odd	1	-3.868 75	3.2825	0.143 75	0.1375

approximation, almost as two independent atoms [15] that are described by the base parameters $\{0.5, -0.5, 0.5, 0.5\}$, these values were used as starting values for the optimization. The lowest ground-state energy at $R = 5.0 a_0$ found this way with $\Omega = 10$ was obtained with the base parameters listed in the first row of Table I. The choice of the start parameters of the second base that should provide a good description for small interhadronic separations is less straightforward, if one does not want to represent a free positronium but the excited molecular states. After some trials, the same start parameters as for the first base (representing independent H and $\bar{H}$ atoms) were also used as a starting point for the second base $\{y_1, x_1, u_1, w_1\}$. However, now the energy of the second excited state is optimized. Most importantly, the optimization starts at $R = 5.0 a_0$, but the optimal parameters found at this value of R only serve as a starting point to find the optimal parameters at $R = 0.8 a_0$. The latter are found by decreasing R in small steps and using the corresponding optimized parameters as a starting point (for the four-dimensional gradient descent algorithm) at the next R value. With the aid of this iterative procedure, finally the optimized base parameters $\{y_1, x_1, u_1, w_1\}$ at $R = 0.8 a_0$ listed in the second row of Table I were determined. An analogous procedure was applied in order to find the optimized parameters of the two bases used in the calculations of the states with Q -odd symmetry, listed in the third and fourth rows of Table I. However, in this case the first and not the second excited state was used when determining the base parameters of the second basis. It turns out that the introduction of the second base that is optimized for the excited state is also crucial for obtaining free positronium states, as is discussed in more detail below.

C. Hadronic problem

Once the leptonic problem is solved the obtained Born-Oppenheimer curves can be used to solve the hadronic Schrödinger equation, yielding the total rovibronic (rotational, vibrational, and leptonic) energies of the $H\bar{H}$ molecule within the Born-Oppenheimer approximation. However, as is discussed below, the excited leptonic states of $H\bar{H}$ show numerous avoided crossings and it was decided to use manually diabaticized states, i.e., quasi-diabatic instead of adiabatic states, for obtaining the solutions of the hadronic problem. To simplify the notion, in the following the phrases "diabaticized state" and "diabatic state" are used synonymously for those states that preserve their character when passing over an avoided crossing and that were obtained by an approximate manual diabaticization. Analogously, the character-changing states are called Born-Oppenheimer or adiabatic states, even though adiabatic corrections are not considered.

In the absence of an external potential the Hamiltonian for the nuclear motion is isotropic and thus the angular solutions of $\chi_{v,J,m_J}^{(m)}(\vec{R})$ in Eq. (4) are given by the spherical harmonics $Y_{J,m_J}(\theta_R, \varphi_R)$, with the two angles θ_R and φ_R describing the orientation of the interhadronic separation vector $\vec{R}$. J is the rotational quantum number, every rotational state being $2J + 1$ times degenerate. The remaining one-dimensional radial equation describing vibrational (or dissociative) motion within one Born-Oppenheimer potential $V_m(R)$ can be solved numerically in various ways. In this work the radial wave function is expanded in a B -spline basis yielding a generalized eigenvalue problem. An advantage of the basis-set expansion is that, depending on the adopted number of B splines, a large number of rovibrational solutions are obtained simultaneously. A total of 2048 B splines of order $k = 15$, distributed over a linear knot sequence between $R_0 = 0 a_0$ and $R_{\max} = 5.0 a_0$, were found to provide sufficiently converged results.

Within the Born-Oppenheimer approximation adopted here there is the intricate question of how the potentials curves should be continued below the critical distance, since the nonadiabatic corrections diverge [34], as was already mentioned. This is evidently directly connected to the question of whether the critical distance is caused by a Feshbach-type resonance between a molecular state and the free positronium-protonium pair or by a continuous change of the state [15,16,34]. Adopting the latter assumption, every Born-Oppenheimer potential represents one state completely, and its leptonic energy $E_{\text{lep},m}(R)$ should converge for small values of R to the energies of a free positronium. The leptonic energies were thus correspondingly extrapolated below $R = 0.8 a_0$. This value slightly above the most accurate value reported for the critical distance ($R_c = 0.744 a_0$ [33]) was chosen for two reasons. First, the basis sets adopted in this work start to deviate visibly from the best available ground-state curve in Ref. [33] at around this value of R . Second, it was concluded in Ref. [34] that the adiabatic approximation should become inadequate between $R = 0.8 a_0$ and $1.0 a_0$. The sensitivity of the obtained rovibronic energies on the exact form of the extrapolation was checked by testing rather different functional forms and was found to be very small. In view of the adopted approximations, starting with the Born-Oppenheimer approximation, the uncertainty induced by the extrapolation below the critical value thus appears to be negligible, since the present work does not strive for spectroscopic data for single rovibronic states, but investigates the density of rovibronic states close to the dissociation threshold of the leptonic ground state. Thus, in the end, a simple linear extrapolation was used for the results shown in this work, but in Fig. 9 a comparison of the results obtained with either linear or a sixth-order polynomial are also given.

An additional practical problem arises, because the Born-Oppenheimer potentials are precalculated at a finite number N of interhadronic separations R_i , $i = 1, N$. However, the numerical integration that is performed when solving the Schrödinger equation, in the present case when setting up the Hamiltonian matrix in the B -spline basis, typically requires the values at arbitrary R values (within the interval $[R_0, R_{\max}]$). The interpolation between the discrete set of R_i values is usually rather straightforward and in the present approach a cubic spline interpolation is adopted.

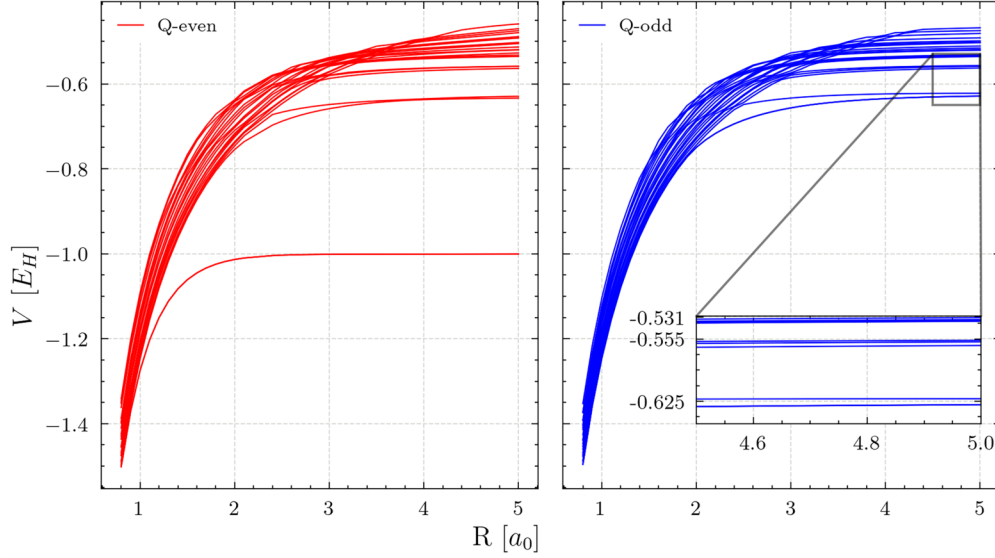


FIG. 2. Lowest-lying Born-Oppenheimer potential curves of $H\bar{H}$ (in Hartree) as a function of the interhadronic separation R (in Bohr) for the Σ states that possess Q -even (left, red) or Q -odd (right, blue) symmetry. The inset shows a zoom that more clearly reveals the asymptotic behavior of the low-lying Q -odd states. (The data points are connected by lines for guiding the eye. The basis sets described in Sec. III B with $\Omega = 10$ were adopted.)

However, from the attractive interhadronic interaction term ($V_{p,\bar{p}} = -1/R$) in the leptonic Hamiltonian it is clear that all $H\bar{H}$ potential curves $V_m(R)$ diverge for $R \rightarrow 0 a_0$. This evidently leads to numerical problems, if the integrals of the potential-energy operator between the B splines close to $R_0 = 0 a_0$ are calculated. Stable solutions were found when using the function

$$V_{\text{ext}}(R) = -A - B \exp(-CR) \quad (9)$$

within the interval $[R_0, 10^{-6} a_0]$. The same coefficients ($A = 4.545\,473 \times 10^4$, $B = 1.294\,251 \times 10^5$, and $C = 3.044\,522 \times 10^6$) were used, since in that small R range close to zero the function is completely dominated by the interhadronic interaction term that is identical for all states. It was checked that the artificial extrapolation that enforces a finite value at $R \rightarrow 0 a_0$ has a negligible effect on the calculated energies that is much smaller than the already small impact of the extrapolation in the interval $[10^{-6} a_0, 0.8 a_0]$. The reason is that all wave functions are localized at much larger values of R than $R = 10^{-6} a_0$.

IV. RESULTS

A. Leptonic energy spectrum

The Born-Oppenheimer potential curves V obtained using the bases in Table I and $\Omega = 10$ are presented in Fig. 2 for both Q -even and Q -odd states, though separately. (The numerical values of the ten lowest states of each symmetry are given in Tables III and IV of Appendix B.) Expectedly, all states are clearly dominated by the attractive interhadronic potential and thus basically go as $-1/R$ to $-\infty$ as R approaches zero. This is equally true for both Q -even and Q -odd states. Therefore, all states should support (numerous) rovibrational states where the low-lying ones should be very similar to protonium states. This finding contradicts the claim in Ref. [46], where it is

stated that the potential curves corresponding to odd states need not to be considered, since they “increase monotonically as the internuclear distance R decreases.” Therefore, Q -odd states cannot *per se* be neglected in collision processes, except for reasons of symmetry conservation.

In the limit of separated atoms there are $2n$ degenerate excited states, each with the energy of $-(1 + 1/(n+1)^2)/2$, which are the energies of one of the (anti)atoms being in the ground state and one (anti)atom being excited to a state with principal quantum number n . The obtained leptonic potential curves of the excited states approach these energies with the expected degeneracies, as can be seen in the inset of Fig. 2.

A clearer picture is obtained if the dominant $-1/R$ term is subtracted and the leptonic energy curves E_{lep} are considered, see Fig. 3. Also shown is the (to the authors’ knowledge) most accurate ground-state potential curve [33], to which the present result agrees very well: the relative deviations are 3.7×10^{-5} at $R = 0.8 a_0$ and 4.3×10^{-8} at $R = 5.0 a_0$. (Due to the more sparse data set in Ref. [33] and the linear interpolation, it falsely appears as the present results are lower between $R = 4.0$ and $5.0 a_0$, but they lie consistently above.) Since there are no further data available to which the excited-state results can be compared, convergence studies with respect to Ω were performed. They are shown for $R = 0.8 a_0$ and $5.0 a_0$ in Figs. 4 and 5, respectively. For $\Omega = 10$ all states are converged up to the percent level, mostly even much better. In

TABLE II. Base symmetries.

Basis set	Base
James-Coolidge symmetric	$y = x = 0 \wedge u = w$
James-Coolidge asymmetric	$y = x = 0 \wedge u \neq w$
H_2	$y = -x = u = w$
H^-H^+	$y = x = u = w$

TABLE III. Born-Oppenheimer potential curves (in Hartree) for the ten lowest-lying Σ states ($n = 0$ to $n = 9$) with Q -even symmetry. (The interhadronic separations R are given in Bohr units a_0 .)

R	$n = 0$	$n = 1$	$n = 2$	$n = 3$	$n = 4$	$n = 5$	$n = 6$	$n = 7$	$n = 8$	$n = 9$
0.8	-1.501 279	-1.495 951	-1.489 710	-1.487 174	-1.475 321	-1.473 540	-1.467 338	-1.454 995	-1.453 036	-1.436 223
1.0	-1.274 441	-1.247 239	-1.239 823	-1.239 344	-1.226 919	-1.225 048	-1.217 280	-1.208 463	-1.203 493	-1.186 224
1.1	-1.203 236	-1.156 483	-1.149 193	-1.148 631	-1.136 884	-1.134 174	-1.126 333	-1.118 905	-1.112 659	-1.095 441
1.2	-1.150 521	-1.080 825	-1.073 741	-1.072 903	-1.061 828	-1.058 426	-1.050 535	-1.044 307	-1.036 973	-1.020 691
1.3	-1.111 461	-1.016 808	-1.009 928	-1.008 800	-0.998 371	-0.994 327	-0.986 390	-0.981 301	-0.972 951	-0.958 115
1.4	-1.082 505	-0.961 953	-0.955 299	-0.953 845	-0.944 105	-0.939 384	-0.931 403	-0.927 491	-0.918 106	-0.904 780
1.5	-1.061 035	-0.914 453	-0.908 077	-0.906 212	-0.897 283	-0.891 769	-0.883 755	-0.881 111	-0.870 617	-0.858 846
1.6	-1.045 120	-0.872 970	-0.866 967	-0.864 529	-0.856 606	-0.850 112	-0.842 126	-0.840 765	-0.829 125	-0.818 906
1.7	-1.033 332	-0.836 547	-0.831 031	-0.827 746	-0.821 060	-0.813 364	-0.805 966	-0.804 856	-0.792 604	-0.783 823
1.8	-1.024 610	-0.804 630	-0.799 524	-0.795 046	-0.789 741	-0.780 712	-0.774 625	-0.772 268	-0.760 300	-0.752 687
1.9	-1.018 170	-0.777 261	-0.771 516	-0.765 784	-0.761 764	-0.751 521	-0.746 661	-0.742 999	-0.731 869	-0.724 895
2.0	-1.013 428	-0.754 619	-0.745 980	-0.739 446	-0.736 406	-0.725 302	-0.721 376	-0.716 654	-0.709 675	-0.702 571
2.1	-1.009 947	-0.736 071	-0.722 550	-0.715 615	-0.713 240	-0.701 892	-0.698 427	-0.696 293	-0.692 602	-0.680 558
2.4	-1.004 216	-0.697 160	-0.672 293	-0.663 384	-0.655 974	-0.654 580	-0.642 020	-0.640 141	-0.633 018	-0.624 937
2.5	-1.003 256	-0.688 019	-0.666 591	-0.646 754	-0.639 284	-0.638 048	-0.625 665	-0.623 908	-0.616 519	-0.612 151
2.6	-1.002 572	-0.680 219	-0.661 780	-0.631 393	-0.623 879	-0.622 788	-0.611 472	-0.609 056	-0.603 059	-0.599 830
2.7	-1.002 088	-0.673 531	-0.657 699	-0.617 167	-0.609 655	-0.608 744	-0.601 313	-0.595 188	-0.591 683	-0.590 968
2.8	-1.001 749	-0.667 769	-0.654 224	-0.603 982	-0.597 385	-0.596 039	-0.593 433	-0.586 953	-0.583 880	-0.581 767
2.9	-1.001 512	-0.662 789	-0.651 255	-0.592 280	-0.590 564	-0.583 958	-0.583 413	-0.582 345	-0.580 259	-0.569 698
3.0	-1.001 348	-0.658 470	-0.648 709	-0.587 360	-0.580 452	-0.579 750	-0.577 602	-0.572 287	-0.571 010	-0.558 339
3.2	-1.001 153	-0.651 444	-0.644 633	-0.581 347	-0.575 057	-0.573 029	-0.559 117	-0.552 510	-0.551 414	-0.550 236
3.3	-1.001 093	-0.648 592	-0.642 999	-0.579 023	-0.572 960	-0.571 152	-0.550 433	-0.549 389	-0.547 967	-0.546 905
3.4	-1.001 048	-0.646 106	-0.641 576	-0.577 021	-0.571 124	-0.569 511	-0.548 360	-0.546 172	-0.545 023	-0.541 351
3.5	-1.001 010	-0.643 943	-0.640 328	-0.575 283	-0.569 510	-0.568 072	-0.546 731	-0.544 562	-0.543 330	-0.539 134
3.6	-1.000 976	-0.642 071	-0.639 218	-0.573 765	-0.568 089	-0.566 806	-0.545 311	-0.543 126	-0.541 794	-0.537 082
3.7	-1.000 943	-0.640 474	-0.638 206	-0.572 431	-0.566 832	-0.565 690	-0.544 060	-0.541 840	-0.540 387	-0.535 171
3.8	-1.000 911	-0.639 144	-0.637 248	-0.571 254	-0.565 719	-0.564 705	-0.542 952	-0.540 681	-0.539 084	-0.533 386
3.9	-1.000 878	-0.638 077	-0.636 307	-0.570 211	-0.564 728	-0.563 835	-0.541 966	-0.539 631	-0.537 867	-0.531 720
4.0	-1.000 843	-0.637 241	-0.635 378	-0.569 283	-0.563 845	-0.563 065	-0.541 085	-0.538 675	-0.536 721	-0.530 169
4.1	-1.000 807	-0.636 579	-0.634 486	-0.568 453	-0.563 055	-0.562 383	-0.540 294	-0.537 800	-0.535 632	-0.528 730
4.2	-1.000 770	-0.636 040	-0.633 653	-0.567 709	-0.562 346	-0.561 778	-0.539 580	-0.536 996	-0.534 591	-0.527 403
4.3	-1.000 733	-0.635 589	-0.632 892	-0.567 037	-0.561 709	-0.561 241	-0.538 933	-0.536 254	-0.533 590	-0.526 192
4.4	-1.000 694	-0.635 205	-0.632 203	-0.566 430	-0.561 134	-0.560 764	-0.538 343	-0.535 566	-0.532 623	-0.525 101
4.5	-1.000 656	-0.634 871	-0.631 581	-0.565 878	-0.560 615	-0.560 339	-0.537 801	-0.534 927	-0.531 686	-0.524 127
4.6	-1.000 618	-0.634 579	-0.631 023	-0.565 374	-0.560 144	-0.559 960	-0.537 300	-0.534 331	-0.530 776	-0.523 251
4.7	-1.000 580	-0.634 319	-0.630 521	-0.564 912	-0.559 717	-0.559 622	-0.536 831	-0.533 775	-0.529 892	-0.522 443
4.8	-1.000 543	-0.634 086	-0.630 070	-0.564 487	-0.559 333	-0.559 316	-0.536 390	-0.533 253	-0.529 034	-0.521 675
4.9	-1.000 507	-0.633 874	-0.629 664	-0.564 094	-0.559 050	-0.558 974	-0.535 970	-0.532 765	-0.528 203	-0.520 928
5.0	-1.000 473	-0.633 679	-0.629 299	-0.563 730	-0.558 807	-0.558 651	-0.535 566	-0.532 306	-0.527 399	-0.520 192

the absence of reference data, the shown relative error is thus defined with respect to the most accurate calculation ($\Omega = 10$), i.e., as $[E(m, 10) - E(m, \Omega)]/E(m, 10)$ [51]. At least for sufficiently large values of Ω an exponential decrease of the error can be seen. While the ground state is converged up to the $\mathcal{O}(10^{-3})$ for interhadronic distances below $R = 2.0 a_0$ and up to $\mathcal{O}(10^{-7})$ for $R > 2.0 a_0$, higher excited states are less and less well converged. This, as well as the later onset of the exponential improvement, is somehow expected, since with the level of excitation the number of nodes increases. Their proper representation requires correspondingly polynomials of higher order and thus larger Ω values.

The leptonic energy spectrum clearly shows a large number of avoided crossings between two kinds of states. For both symmetries these avoided crossings are clearly visible starting from the $m = 2$ states. For the two lower excited $m = 1$ states no clear avoided crossing can be seen (at $R \approx 2.0 a_0$).

These two states behave in that respect very similar to the ($m = 0$) ground state. Accordingly, the present results for the $m = 1$ states are also inconclusive with respect to the question of whether these states continuously change their character from $H\bar{H}$ to protonium and positronium, or if a more precise calculation would reveal avoided crossings. This important question requests further investigations beyond the scope of this work. Leaving out the ground state, the spectra for Q -even and Q -odd states look very similar at first glance. States that decrease in energy for increasing interhadronic separation R are repeatedly "crossed" by states with almost constant energy, leading to the large number of avoided crossings. It is noteworthy that the slope of the R -dependent states is also very similar, only slowly decreasing with increasing excitation m . As for the ground state, the increasing energy for decreasing R is a consequence of the fact that as H and $\bar{H}$ approach each other, the energy gain due to the larger overlap of the

TABLE IV. As Table III, but for states with Q -odd symmetry.

R	$n = 0$	$n = 1$	$n = 2$	$n = 3$	$n = 4$	$n = 5$	$n = 6$	$n = 7$	$n = 8$	$n = 9$
0.8	-1.495 716	-1.488 765	-1.486 060	-1.476 993	-1.473 624	-1.468 267	-1.460 019	-1.453 327	-1.446 747	-1.439 091
1.0	-1.245 597	-1.238 857	-1.235 332	-1.227 564	-1.223 610	-1.216 239	-1.210 941	-1.204 735	-1.196 119	-1.188 518
1.1	-1.154 622	-1.147 960	-1.144 035	-1.136 869	-1.132 599	-1.124 268	-1.120 474	-1.114 345	-1.104 746	-1.098 180
1.2	-1.078 798	-1.072 206	-1.067 882	-1.061 296	-1.056 718	-1.047 468	-1.045 117	-1.039 000	-1.028 487	-1.022 983
1.3	-1.014 628	-1.008 112	-1.003 387	-0.997 374	-0.992 504	-0.982 581	-0.981 185	-0.975 235	-0.963 994	-0.959 339
1.4	-0.959 619	-0.953 195	-0.948 072	-0.942 637	-0.937 502	-0.927 719	-0.925 656	-0.920 574	-0.908 979	-0.904 580
1.5	-0.911 943	-0.905 648	-0.900 147	-0.895 304	-0.889 940	-0.880 732	-0.877 144	-0.873 155	-0.861 721	-0.856 751
1.6	-0.870 235	-0.864 152	-0.858 334	-0.854 058	-0.848 524	-0.839 905	-0.834 757	-0.831 449	-0.820 693	-0.814 573
1.7	-0.833 468	-0.827 792	-0.821 830	-0.817 823	-0.812 239	-0.803 979	-0.797 643	-0.794 206	-0.784 595	-0.777 203
1.8	-0.800 908	-0.796 116	-0.790 128	-0.785 501	-0.780 128	-0.771 894	-0.764 891	-0.760 664	-0.752 445	-0.744 008
1.9	-0.772 410	-0.768 889	-0.762 087	-0.756 250	-0.751 333	-0.742 911	-0.735 656	-0.730 378	-0.723 539	-0.714 451
2.0	-0.749 520	-0.743 916	-0.736 460	-0.729 691	-0.725 280	-0.716 583	-0.709 346	-0.702 963	-0.697 396	-0.688 072
2.1	-0.731 616	-0.720 372	-0.712 948	-0.705 540	-0.701 599	-0.692 601	-0.685 561	-0.678 156	-0.675 376	-0.672 553
2.2	-0.716 923	-0.698 758	-0.691 427	-0.683 520	-0.680 017	-0.670 816	-0.666 444	-0.663 609	-0.655 333	-0.651 448
2.3	-0.704 631	-0.678 966	-0.671 724	-0.663 434	-0.660 681	-0.658 906	-0.650 450	-0.644 104	-0.634 835	-0.631 610
2.4	-0.694 241	-0.660 805	-0.654 263	-0.652 928	-0.644 843	-0.642 029	-0.632 155	-0.626 150	-0.617 227	-0.613 529
2.5	-0.685 396	-0.648 701	-0.644 034	-0.636 891	-0.627 915	-0.625 399	-0.615 640	-0.609 892	-0.604 815	-0.600 794
2.6	-0.677 824	-0.644 516	-0.628 606	-0.621 582	-0.612 506	-0.610 090	-0.602 250	-0.596 269	-0.595 551	-0.592 407
2.7	-0.671 311	-0.641 024	-0.614 320	-0.607 564	-0.599 509	-0.596 059	-0.592 868	-0.590 285	-0.583 718	-0.582 637
2.8	-0.665 688	-0.638 082	-0.601 121	-0.595 540	-0.590 677	-0.586 563	-0.582 986	-0.581 067	-0.579 965	-0.569 714
2.9	-0.660 816	-0.635 595	-0.589 980	-0.587 512	-0.583 026	-0.580 275	-0.576 920	-0.570 715	-0.569 063	-0.560 288
3.0	-0.656 583	-0.633 486	-0.585 221	-0.579 760	-0.576 711	-0.574 246	-0.569 273	-0.559 738	-0.557 746	-0.555 656
3.1	-0.652 896	-0.631 693	-0.582 075	-0.576 958	-0.571 918	-0.565 992	-0.558 810	-0.554 147	-0.552 363	-0.551 810
3.2	-0.649 679	-0.630 166	-0.579 495	-0.574 555	-0.569 892	-0.555 915	-0.552 071	-0.550 142	-0.549 524	-0.548 094
3.3	-0.646 867	-0.628 864	-0.577 303	-0.572 467	-0.568 134	-0.549 862	-0.548 145	-0.547 521	-0.546 223	-0.544 523
3.4	-0.644 405	-0.627 751	-0.575 411	-0.570 644	-0.566 603	-0.547 957	-0.546 383	-0.545 771	-0.542 881	-0.537 319
3.5	-0.642 248	-0.626 802	-0.573 765	-0.569 048	-0.565 267	-0.546 352	-0.544 855	-0.544 235	-0.541 434	-0.531 106
3.6	-0.640 356	-0.625 990	-0.572 324	-0.567 648	-0.564 099	-0.544 956	-0.543 512	-0.542 881	-0.540 159	-0.529 711
3.7	-0.638 695	-0.625 298	-0.571 055	-0.566 416	-0.563 077	-0.543 730	-0.542 326	-0.541 684	-0.539 031	-0.528 507
3.8	-0.637 236	-0.624 709	-0.569 934	-0.565 330	-0.562 180	-0.542 648	-0.541 276	-0.540 624	-0.538 031	-0.527 447
3.9	-0.635 954	-0.624 209	-0.568 939	-0.564 371	-0.561 394	-0.541 688	-0.540 345	-0.539 683	-0.537 143	-0.526 510
4.0	-0.634 828	-0.623 786	-0.568 053	-0.563 522	-0.560 703	-0.540 835	-0.539 517	-0.538 845	-0.536 353	-0.525 677
4.1	-0.633 837	-0.623 432	-0.567 261	-0.562 769	-0.560 097	-0.540 073	-0.538 778	-0.538 097	-0.535 648	-0.524 935
4.2	-0.632 964	-0.623 136	-0.566 552	-0.562 101	-0.559 564	-0.539 390	-0.538 118	-0.537 428	-0.535 017	-0.524 272
4.3	-0.632 197	-0.622 893	-0.565 914	-0.561 506	-0.559 095	-0.538 778	-0.537 528	-0.536 828	-0.534 452	-0.523 678
4.4	-0.631 520	-0.622 696	-0.565 339	-0.560 975	-0.558 683	-0.538 226	-0.536 998	-0.536 289	-0.533 945	-0.523 144
4.5	-0.630 924	-0.622 540	-0.564 818	-0.560 502	-0.558 321	-0.537 728	-0.536 522	-0.535 804	-0.533 489	-0.522 663
4.6	-0.630 398	-0.622 418	-0.564 345	-0.560 078	-0.558 002	-0.537 278	-0.536 093	-0.535 366	-0.533 079	-0.522 229
4.7	-0.629 933	-0.622 328	-0.563 915	-0.559 698	-0.557 722	-0.536 869	-0.535 707	-0.534 970	-0.532 708	-0.521 836
4.8	-0.629 523	-0.622 266	-0.563 522	-0.559 357	-0.557 476	-0.536 496	-0.535 358	-0.534 611	-0.532 374	-0.521 480
4.9	-0.629 160	-0.622 227	-0.563 162	-0.559 051	-0.557 260	-0.536 157	-0.535 042	-0.534 285	-0.532 071	-0.521 157
5.0	-0.628 839	-0.622 209	-0.562 832	-0.558 775	-0.557 070	-0.535 846	-0.534 756	-0.533 989	-0.531 796	-0.520 862

wave functions of the electron and the positron is overcompensated by the repulsion of the electron (positron) and the antiproton (proton) and thus the reduced binding energy to the hadrons. Evidently, the almost constant energies observed for the other manifold of states as a function of R and thus the independence on the R is a strong indication that these states represent (discretized) free positronium states. A further validation of this interpretation is given in the following Sec. IV B.

Interestingly, the Q -odd manifold also contains states that, diabatically continued, increase in energy as R increases. This is clearly in contrast to the behavior of the other states. As a guide to the eye, the diabatic state with the largest slope is highlighted (black line in Fig. 3), together with a diabatic state

that shows the “usual” behavior as is known from the ground state. A more detailed analysis beyond the scope of this work would be needed in order to find a possible explanation (and to rule out that these states with positive slope are just an artifact of an insufficient basis set). The mentioned two exemplary shown diabatic states were obtained by resolving the avoided crossings manually such that the “character” of the state (increasing, decreasing, or constant in energy) is preserved, turning avoided crossings into true crossings. For example, the second-highest Q -odd state at $R = 5.0 a_0$ increases in energy for decreasing R until about $R = 2.5 a_0$, at which the adiabatic state changes its slope and character drastically as its energy becomes almost constant. On the other hand, the diabatic state continues smoothly through this and numerous subsequent

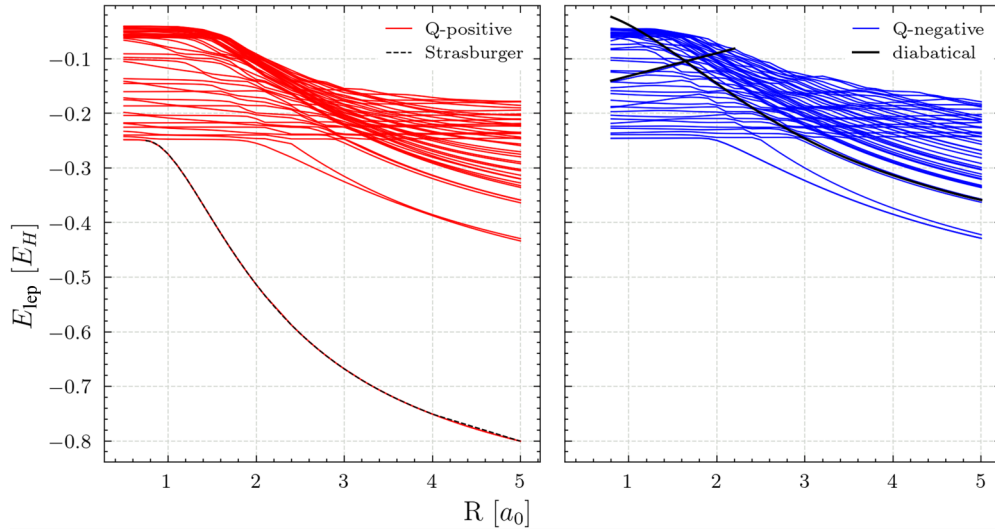


FIG. 3. The same as Fig. 2, but showing the lepton energies E_{lep} instead of the potential curves V . Also shown is the ground state obtained by Strasburger [33] (left, black dashed) and two diabatic states, sketched manually for guiding the eye (right, black solid).

crossings. Its visibility in the form of avoided crossings with states of almost constant energy is enhanced by the shown high density of states [52].

B. Discretized positronium states

As was mentioned before, earlier studies have shown that the theoretical description of collisions between anti-hydrogen and hydrogen require the inclusion of states that describe the rearrangement into positronium and protonium, optimally in a close-coupling framework. In the earlier studies of these collisions using Kołos-Wolniewicz wave functions the calculations did not show signatures of states describing free positronium. Therefore, T -matrix elements describing the rearrangement channel were calculated by obtaining the wave functions in the final positronium channel setting the hadronic charges to zero [20,22]. Alternatively, the positronium wave function was obtained numerically [26]. Clearly, it would be very attractive to obtain the wave functions of the rearrangement process, i.e., the molecular $\text{H}\bar{\text{H}}$ states

as well as the (discretized) free positronium states within a single diagonalization of the complete Hamiltonian, as is the case in full four-body calculations. As was discussed in Sec. IV A, the present calculation does not only reveal states that show the expected behavior of molecular $\text{H}\bar{\text{H}}$ states (similar to the ground state) but also states with energies almost independent of R , which is a strong indication that they are, in fact, the sought-for positronium states. It is noteworthy that, adopting only a single-base basis set, no constant-energy states were observed, as in earlier calculations adopting Kołos-Wolniewicz basis functions. While these two findings (R -independent energy and the appearance only with the use of a dual-base basis set) is already a strong indication, a further validation was made.

As is well known, continuum states can be discretized by enclosing the quantum system into a box with infinite walls. The energies of the continuum states increase quadratically with the box size, while those of bound states are box-size independent, once the box is sufficiently large to fully contain the state. Within the present approach, the effect of an enclosing box can be emulated by a simultaneous scaling of some exponents of the basis functions, i.e., of the base. More accurately, it is the radial coordinate that should be scaled, and thus within the prolate-spheroidal coordinates adopted here it is the ξ coordinate. Thus, the base parameters u and w are

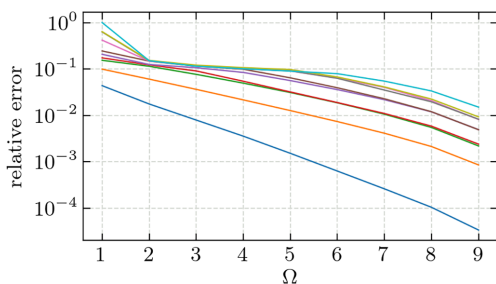


FIG. 4. Convergence study for the ten lowest-lying Q -even Σ states and $R = 0.8 a_0$. The basis set is systematically improved by increasing Ω , see Eq. (7). Shown is the relative error with respect to the results obtained with $\Omega = 10$. The states are, in increasing order, colored as blue ($m = 0$), orange ($m = 1$), green ($m = 2$), red ($m = 3$), purple ($m = 4$), brown ($m = 5$), pink ($m = 6$), gray ($m = 7$), olive ($m = 8$), and cyan ($m = 9$).

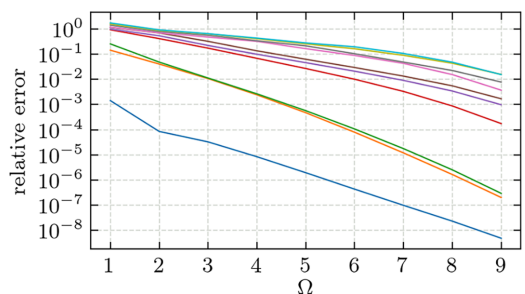


FIG. 5. The same as Fig. 4, but for $R = 5.0 a_0$.

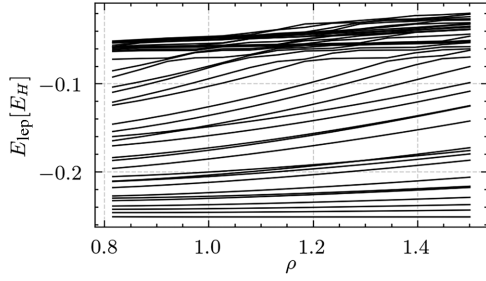


FIG. 6. Energy of Q -even states at $R = 0.8$ as a function of a real scaling parameter ρ .

multiplied with a real scaling parameter ρ ,

$$u(\rho) = \rho u, \quad w(\rho) = \rho w. \quad (10)$$

Figure 6 shows the leptonic energies of the Q -even Σ states at $R = 0.8$ as a function of ρ . The lowest state, the $\text{H}\bar{\text{H}}$ molecular ground state, is basically independent of ρ . However, the states with slightly higher energy show the quadratic dependence on ρ expected for continuum states, in this case states describing a free positronium. At higher energies more states with almost constant energy appear, corresponding to the excited molecular states and showing avoided crossings with the quadratically increasing states. Therefore, these states indeed describe free positronium with additional quanta of kinetic energy.

With the obtained positronium states lifetime calculations for the bound states (more accurately metastable states) should in principle become possible, either directly from the real stabilization graph or, even better, using the complex-scaling method as was, e.g., adopted in the four-body calculations in Refs. [41,42]. Of course, this would be especially interesting for the leptonic ground state, but no avoided crossing of the leptonic ground state with a positronium state can be conclusively observed in the region above or below the critical distance, see Fig. 7. Again, this would be in accordance with the idea that the rearrangement process in the ground state is not due to a Feshbach-type resonance, but due to a continuous transition from the bound into a continuum state. It is worth noting that this seems to be different for collisions occurring on excited-state potential curves, since they show clear avoided crossings.

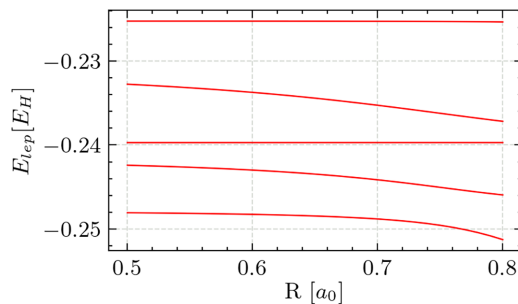


FIG. 7. Leptonic energies of the ground state and four excited states (also Q -even symmetry) for interhadronic separations around the critical distance $R_c = 0.77 a_0$.

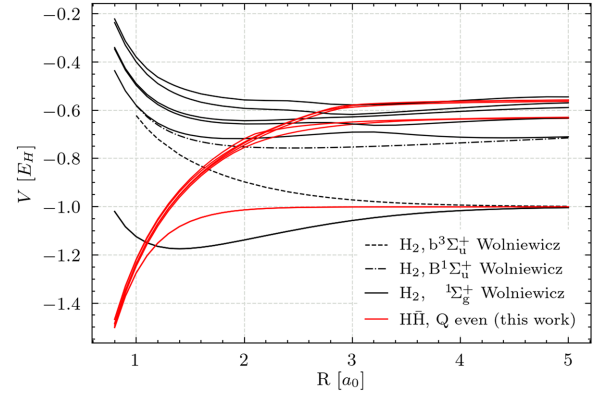


FIG. 8. Comparison of selected Born-Oppenheimer potential curves (Σ symmetry) for H_2 (literature data) and $\text{H}\bar{\text{H}}$ (red curves, this work). For H_2 a selection of lowest-lying $X^1\Sigma_g^+$ (black solid lines, Ref. [53]) states as well as the $b^3\Sigma_u^+$ (black dashed line, Ref. [54]) and the $B^1\Sigma_u^+$ (black chain line, Ref. [55]) states are shown.

C. H-H vs $\bar{\text{H}}$ -H collisions

In order to highlight the role of the excited leptonic states of $\text{H}\bar{\text{H}}$ for antihydrogen-hydrogen collisions, it is instructive to compare this to the collisions between two hydrogen atoms. Figure 8 shows the lowest-lying Q -even potential curves obtained in this work with some of the very precisely known potential curves of H_2 . Within the nonrelativistic approximation adopted here, the collision of a ground-state H atom with either another H atom or an $\bar{\text{H}}$ atom, both also being in their ground states, would start at the same energy: $-1.0 E_H + E_{\text{kin}}$, where E_{kin} is the translation energy of the two atoms. For small collision energies E_{kin} there is in the case of H_2 only a single energetically accessible excited state, the triplet $b^3\Sigma_u^+$, to which the coupling is very small, as it involves a spin flip and relativistic effects are very small for light atoms. All the other excited states are separated from the ground state by an energy gap of some electronvolts and are thus not energetically accessible for small collision energies. This is completely different for $\text{H}\bar{\text{H}}$, where in fact for all Born-Oppenheimer excited-state curves one has $V \rightarrow -\infty$ for $R \rightarrow 0$. Therefore, in principle, *all* excited leptonic states become degenerate with $-1.0 E_H + E_{\text{kin}}$ at some interhadronic separation R , independent of the collision energy $E_{\text{kin}} \geq 0$. It should be emphasized that here not only the earlier considered leptonic states describing the protonium and positronium rearrangement channel are meant, but also those “molecular” states that correspond asymptotically to one (or both) atoms in an excited state. Evidently, a quantitative treatment of possible leptonic excitations needs to be performed in accurate scattering calculations of ground-state H- $\bar{\text{H}}$ collisions.

The impact of the excited leptonic states is expected to be especially large, if the H and $\bar{\text{H}}$ ground-state atoms in the incoming collision channel are energetically degenerate with some rovibrational state of a leptonically excited molecular state, i.e., if a scattering resonance occurs. Figure 9 shows an excerpt of the rovibrational spectrum, i.e., a selection of rovibrational states for the lowest-lying (adiabatic) leptonic molecular states. Evidently, the excited leptonic states support rovibrational states in the region just above the dissociation

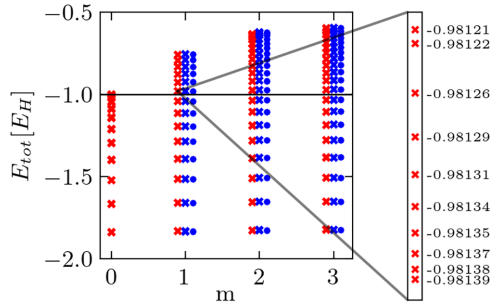


FIG. 9. Spectrum of Q -even (red) and Q -odd (blue) rovibronic states for rotational quantum numbers $J \in 0, \dots, 9$ and different diabaticized leptonic states m . In the case of Q -odd states the results obtained with two different extrapolations of the potential curves at small interhadronic separations, linear (crosses) or using a sixth-order polynomial (dots), are shown. The black line marks the dissociation energy of $H\bar{H}$. Thus, the energy range just above this threshold is most relevant for (low-energy) scattering processes of $\bar{H}$ and H , if both are initially in their ground states. Since the rotational energy spacing is too small to be visible on this scale, the enlarged spectrum in the inset resolves some of the rotational states just above the ground-state dissociation threshold.

threshold that should allow for the occurrence of scattering resonances in $H\text{--}\bar{H}$ -collisions, even for very low collision energies. Considering the plethora of excited leptonic states, a small fraction of which are shown in Fig. 2, it is evident that a large number of resonances occurs, even if only the Q -even states are considered, since the Q -odd states should for symmetry reasons not couple to the Q -even ground state, if CP symmetry is conserved. Note that for sufficiently large collision energies to overcome the centrifugal barrier, also Q -even states of symmetries different from Σ , Π , Δ , ... are expected to lead to resonances in ground-state $H\text{--}\bar{H}$ collisions, as these potential curves also tend to $-\infty$ for $R \rightarrow 0$ [56]. The large density of resonances is, of course, counteracted by the fact that the leptonic coupling matrix elements between the ground state and an excited leptonic state n decrease with increasing n due to the increasing number of nodes of the final-state wave functions. On the other hand, since all molecular $H\bar{H}$ states are metastable due to the open rearrangement channel into protonium and positronium as well as the possibility of leptonic and hadronic annihilation or dipole-allowed radiative relaxation, the rovibronic states possess a finite lifetime and width. Thus, it is expected that the resonance condition is fulfilled at practically any collision energy.

While the main finding of the present work is the occurrence of a high density of resonances in ground-state $H\text{--}\bar{H}$ collisions, but not their exact positions, the uncertainties due to the treatment (extrapolation) below the critical distance may shed some doubt on the findings. The rovibronic ground state of $H\bar{H}$ obtained with the present approach yields an energy of -460.347 a.u., which is very close to the ground-state energy of positronium plus protonium of -459.288 a.u. This is expected, since the Born-Oppenheimer potential curves at small interhadronic separations are dominated by the $1/R$ term and thus the details of the leptonic energies are of minor importance. Therefore, different extrapolations resulted in very similar energies. Nevertheless,

in order to obtain an independent cross-check of the present Born-Oppenheimer treatment (including the extrapolations described above), a full nonrelativistic four-body calculation of the ground-state energy of the $H\bar{H}$ molecule was performed using the code ATOM-MOL-NONBO [57]. The energy obtained from this ansatz is -459.219 a.u. and the relative deviation of the present Born-Oppenheimer calculation is 2.4×10^{-3} . Thus, both treatments are in quite good quantitative agreement, despite the uncertainties from adopting the Born-Oppenheimer approximation and extrapolating the Born-Oppenheimer potential curves. It is worth noting, however, that the four-body code yields a ground-state energy above the positronium-protonium ground state, which is in accordance with the existence of a critical distance, while the present Born-Oppenheimer result would falsely suggest the molecule to be stable against rearrangement into positronium and protonium.

V. CONCLUSION

The Σ spectrum of the $H\bar{H}$ molecule was calculated using Kołos-Wolniewicz basis functions and the Born-Oppenheimer approximation. Adopting a dual-base basis set, i.e., Kołos-Wolniewicz basis sets with two different sets of noninteger exponents, it was possible to reveal free positronium states which repeatedly cross the leptonic bound states, except for the ground and first excited states, leading to a large number of avoided crossings. The ground state (Q even) and the lowest-lying excited states (Q even and Q odd) seem to change their characters around $R = 0.8a_0$ and $R = 2.0a_0$, respectively. However, no conclusive avoided crossing with positronium states was found. Whether the change of character is, in these cases, a continuous change of state character or whether the avoided crossing is not visible due to a deficiency of the adopted basis sets needs further investigation. Extrapolating the leptonic potential curves to interhadronic distances below the critical distance, the rovibronic spectrum was calculated for a number of leptonic states. This calculation is not meant to be of high accuracy, since part of the Born-Oppenheimer potentials were extrapolated and the effects of the strong-force interaction completely ignored. A full four-body calculation of the rovibronic ground state confirmed that the Born-Oppenheimer solutions obtained here appear to be reasonably good, despite the earlier reported breakdown of the Born-Oppenheimer approximation at the critical distance at which the energy of a positronium-protonium system starts to lie below the one of the $H\bar{H}$ molecule. Thus, it can be concluded that besides the already earlier known need for including explicitly the positronium-protonium rearrangement channel into scattering calculations describing $H\text{--}\bar{H}$ collisions, the excited leptonic states and corresponding resonances also need to be considered. The present work is expected to provide a good starting point for such scattering calculations.

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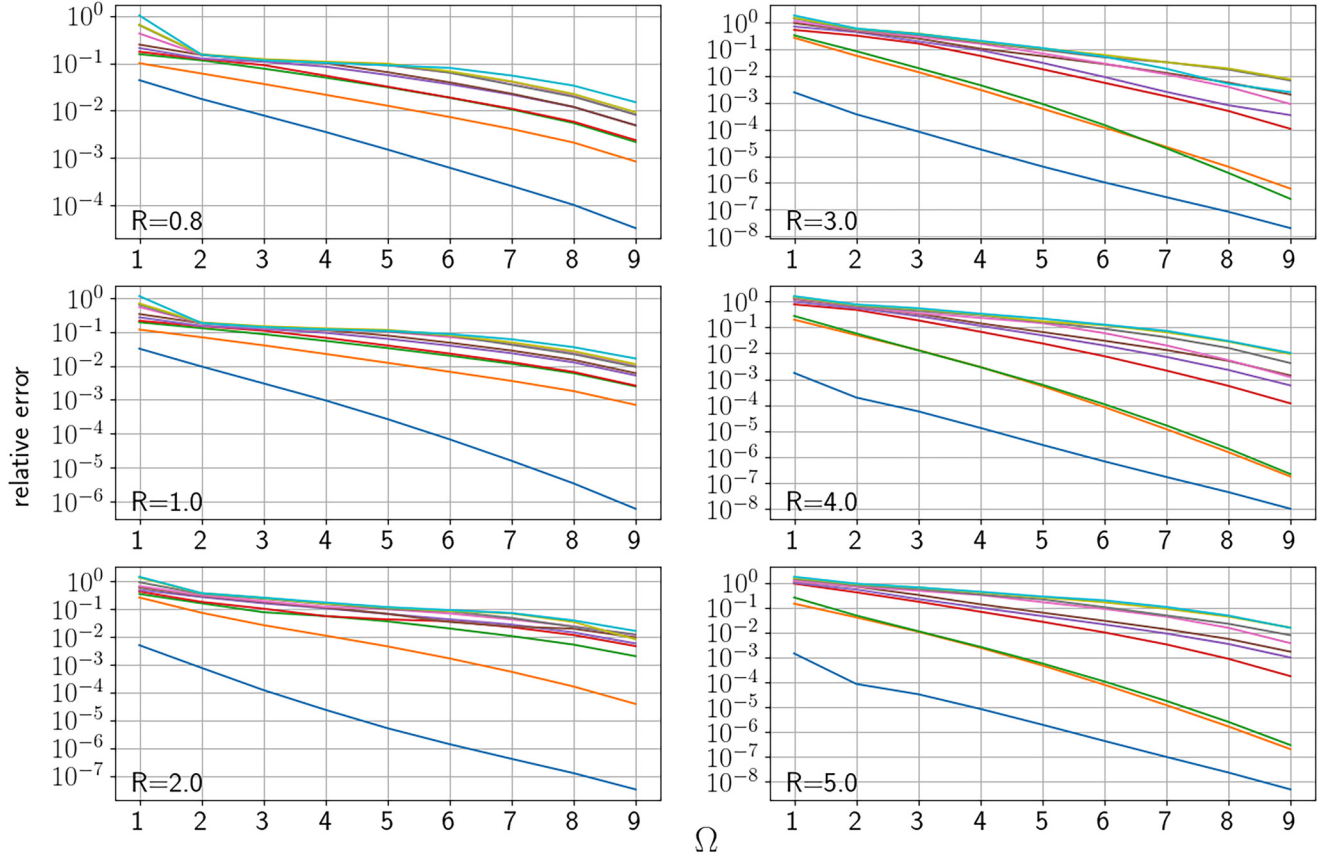


FIG. 10. Relative differences of the Born-Oppenheimer potential curves for Q -positive states at different interhadronic separations to a reference calculation ($\Omega = 10$). The relative difference decreases exponentially as a function of Ω . (The same color coding as in Fig. 4 is used.)

DATA AVAILABILITY

The data that support the findings of this article are not publicly available upon publication because it is not technically feasible and/or the cost of preparing, depositing, and hosting the data would be prohibitive within the terms of this research project. The data are available from the authors upon reasonable request.

APPENDIX A: SYMMETRY-ADAPTED $\mathbf{H}\mathbf{H}$ BASIS FUNCTIONS

Besides the linear dependencies due to the finite numerical precision (which is prevented using variable-precision arithmetics in the modified H2SOLV code adopted in this work [48]), two symmetry-adapted Kołos-Wolniewicz-type basis functions can become identical (and thus linearly dependent) or zero valued (and thus inappropriate) for specific choices of the basis-set parameters. While this problem does not occur for the final bases used in this work for producing the shown results, it can occur during the basis-set optimization in which two of the base parameters may become equal. This problem has been circumvented by removing those basis functions from the basis set that are zero valued (or would occur twice). In this section the construction of symmetry-adapted basis functions avoiding or removing the redundant ones is described. The Kołos-Wolniewicz functions are versatile and

comprise four well-known types of basis sets depending on the symmetry of the base parameters, see Table II [48]. In the following, the names of these basis sets will be used for better readability.

The symmetry-adapted linear combination in Eq. (8),

$$\begin{aligned} \phi_{\mathbf{n}}^{\pm} \propto & \exp(-y\eta_1 - x\eta_2 - u\xi_1 - w\xi_2) \eta_1^{n_1} \eta_2^{n_2} \xi_1^{n_3} \xi_2^{n_4} \\ & \pm (-1)^{n_1+n_2} \exp(+y\eta_2 + x\eta_1 \\ & - u\xi_2 - w\xi_1) \eta_2^{n_1} \eta_1^{n_2} \xi_2^{n_3} \xi_1^{n_4} \end{aligned} \quad (\text{A1})$$

is rewritten here, but omitting the factors of $r_{e\bar{e}}$ and R as they are invariant under the Q -symmetry operation. Whether a basis function is zero valued can be seen directly from Eq. (A1), once a symmetry-adapted base is assumed. To determine whether a basis function might lead to linear dependencies in the overlap matrix, i.e., the brackets of $\phi_{\mathbf{n}}$ with $\phi_{\mathbf{m}}^{\pm}$ and $\phi_{\sigma(\mathbf{m})}^{\pm}$ with $\sigma \in S_4$ have to be inspected. If for a fixed $\phi_{\mathbf{m}}$ two or more permutations $\sigma_1, \sigma_2, \dots$ exist such that $\langle \phi | \phi_{\sigma_1(\mathbf{m})}^{\pm} \rangle = \langle \phi | \phi_{\sigma_2(\mathbf{m})}^{\pm} \rangle$ and $\phi_{\sigma_1(\mathbf{m})}^{\pm}, \phi_{\sigma_2(\mathbf{m})}^{\pm}$ are both contained in the basis, the overlap matrix will contain identical rows.

1. James-Coolidge symmetric

With $y = x = 0 \wedge u = w$ Eq. (A1) simplifies to

$$\begin{aligned} \phi_{\mathbf{m}}^{\pm} \propto & \exp[-u(\xi_1 - \xi_2)] [\eta_1^{m_1} \eta_2^{m_2} \xi_1^{m_3} \xi_2^{m_4} \\ & \pm (-1)^{m_1+m_2} \eta_2^{m_1} \eta_1^{m_2} \xi_2^{m_3} \xi_1^{m_4}] \end{aligned}$$

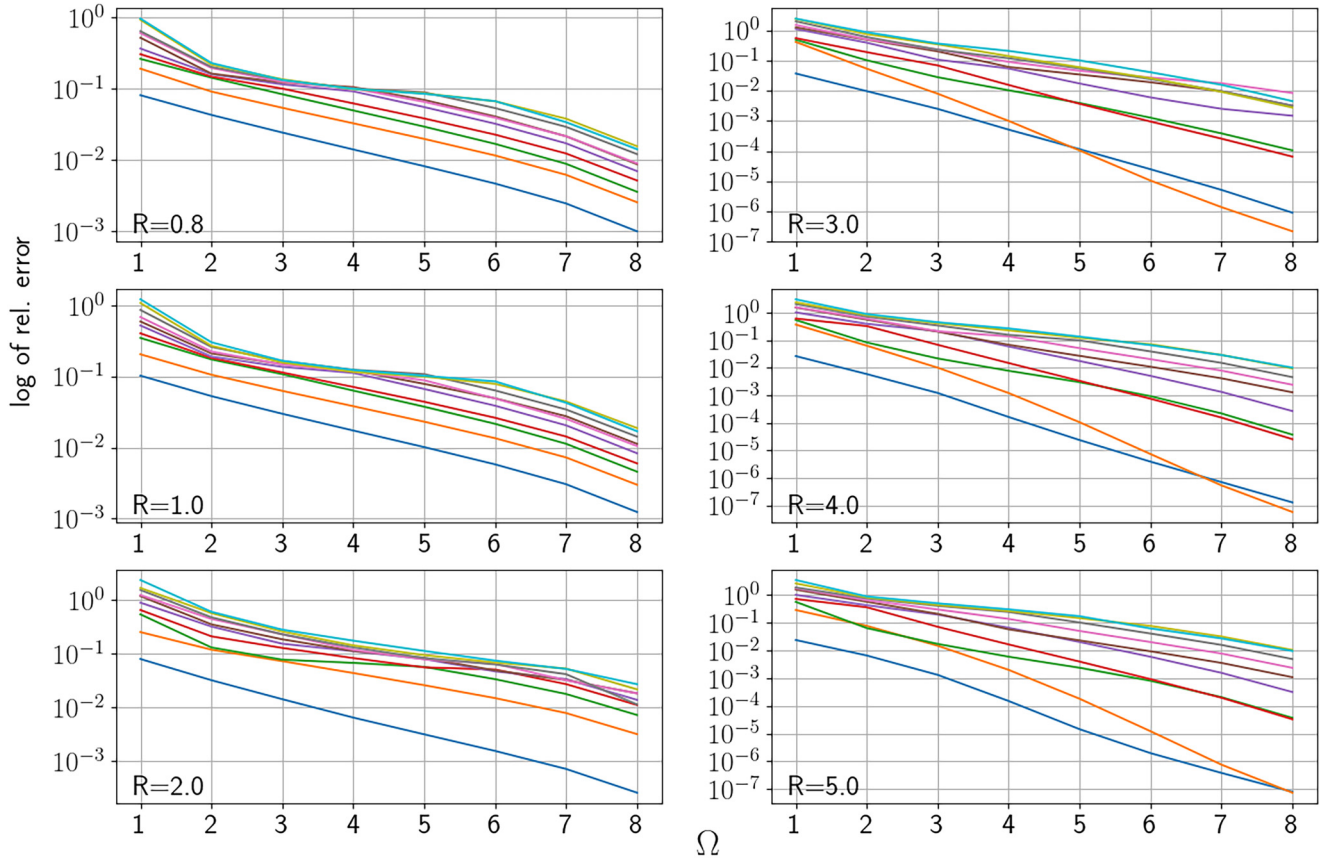


FIG. 11. The same as Fig. 10, but for the ten lowest-lying Q -odd instead of Q -even states. [The states are, in increasing order, blue ($m = 1$), orange ($m = 2$), green ($m = 3$), red ($m = 4$), purple ($m = 5$), brown ($m = 6$), pink ($m = 7$), gray ($m = 8$), olive ($m = 9$), and cyan ($m = 10$).]

and evaluates to zero for $m_1 = m_2 \wedge m_3 = m_4$ and Q -odd symmetry. Linear dependencies, as being caused by

$$\begin{aligned} \langle \phi_{\mathbf{n}} | \phi_{\mathbf{m}}^{\pm} \rangle &= \exp[-2u(\xi_1 + \xi_2)] \\ &\times [\eta_1^{n_1+m_1} \eta_2^{n_2+m_2} \xi_1^{n_3+m_3} \xi_2^{n_4+m_4} \\ &\pm (-1)^{m_1+m_2} \eta_1^{n_1+m_2} \eta_2^{n_2+m_1} \xi_1^{n_3+m_4} \xi_2^{n_4+m_3}], \end{aligned}$$

occur, if m_1, m_2 and m_3, m_4 are permuted, respectively. To obtain a valid basis it has to be restricted according to

$$m_1 > m_3 \vee (m_1 = m_3 \wedge m_3 > m_4)$$

2. James-Coolidge asymmetric

With $y = x = 0 \wedge u = w$ Eq. (A1) simplifies to

$$\begin{aligned} \phi_{\mathbf{m}}^{\pm} &\propto \exp(-u\xi_1 - w\xi_2) \eta_1^{m_1} \eta_2^{m_2} \xi_1^{m_3} \xi_2^{m_4} \\ &\pm (-1)^{m_1+m_2} \exp(-w\xi_1 - u\xi_2) \eta_2^{m_1} \eta_1^{m_2} \xi_2^{m_3} \xi_1^{m_4}, \end{aligned}$$

which will not evaluate to zero. Linear dependencies will not occur as well, as the exponents in

$$\begin{aligned} \langle \phi_{\mathbf{n}} | \phi_{\mathbf{m}}^{\pm} \rangle &= \exp[-2u\xi_1 - 2w\xi_2] \eta_1^{n_1+m_1} \eta_2^{n_2+m_2} \xi_1^{n_3+m_3} \xi_2^{n_4+m_4} \\ &\pm s \exp[-(u+w)(\xi_1 + \xi_2)] \eta_1^{n_1+m_2} \eta_2^{n_2+m_1} \\ &\times \xi_1^{n_3+m_4} \xi_2^{n_4+m_3}, \end{aligned}$$

where $s = (-1)^{m_1+m_2}$, differ.

3. H_2

With $y = -x = u = w$ Eq. (A1) simplifies to

$$\begin{aligned} \phi_{\mathbf{m}}^{\pm} &\propto \exp(y\eta_1 - y\eta_2 - y\xi_1 - y\xi_2) [\eta_1^{m_1} \eta_2^{m_2} \xi_1^{m_3} \xi_2^{m_4} \\ &\pm (-1)^{m_1+m_2} \eta_2^{m_1} \eta_1^{m_2} \xi_2^{m_3} \xi_1^{m_4}], \end{aligned}$$

which again will simplify to zero for $m_1 = m_2 \wedge m_3 = m_4$. Linear dependencies arise due to

$$\begin{aligned} \langle \phi_{\mathbf{n}} | \phi_{\mathbf{m}}^{\pm} \rangle &= \exp[2y(\eta_1 - \eta_2 - \xi_1 - \xi_2)] \\ &[\eta_1^{n_1+m_1} \eta_2^{n_2+m_2} \xi_1^{n_3+m_3} \xi_2^{n_4+m_4} \\ &\pm (-1)^{m_1+m_2} \eta_1^{n_1+m_2} \eta_2^{n_2+m_1} \xi_1^{n_3+m_4} \xi_2^{n_4+m_3}], \end{aligned}$$

for permutations of m_1, m_2 and m_3, m_4 . The same restrictions as for the symmetric James-Coolidge basis have to be applied.

4. H^{-H^+}

With $y = x = u = w$ Eq. (A1) simplifies to

$$\begin{aligned} \phi_{\mathbf{m}}^{\pm} &\propto \exp(-y(\eta_1 + \eta_2 + \xi_1 + \xi_2)) \eta_1^{m_1} \eta_2^{m_2} \xi_1^{m_3} \xi_2^{m_4} \\ &\pm (-1)^{m_1+m_2} \exp(-y(-\eta_1 - \eta_2 + \xi_1 + \xi_2)) \eta_2^{m_1} \eta_1^{m_2} \\ &\times \xi_2^{m_3} \xi_1^{m_4} \end{aligned}$$

which again, due to the different exponential dampening factors, will neither evaluate to zero nor yield linear dependencies.

APPENDIX B: BORN-OPPENHEIMER POTENTIAL CURVES

The numerical values of the ten energetically lowest-lying Σ states of $\text{H}\bar{\text{H}}$ are given in numerical form, both for

Q -even and Q -odd symmetries, in Tables III and IV, respectively. The corresponding convergence studies as a function of the basis-set parameter Ω are shown in Figs. 10 and 11, respectively.

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- [1] G. Baur *et al.*, Production of antihydrogen, *Phys. Lett. B* **368**, 251 (1996).
 - [2] G. Blanford, D. C. Christian, K. Gollwitzer, M. Mandelkern, C. T. Munger, J. Schultz, and G. Zioulas, Observation of atomic antihydrogen, *Phys. Rev. Lett.* **80**, 3037 (1998).
 - [3] M. Amoretti *et al.*, Production and detection of cold antihydrogen atoms, *Nature (London)* **419**, 456 (2002).
 - [4] G. Gabrielse, N. S. Bowden, P. Oxley, A. Speck, C. H. Storry, J. N. Tan, M. Wessels, D. Grzonka, W. Oelert, G. Schepers, T. Seftick, J. Walz, H. Pittner, T. W. Hänsch, and E. A. Hessels, Background-free observation of cold antihydrogen with field-ionization analysis of its states, *Phys. Rev. Lett.* **89**, 213401 (2002).
 - [5] G. Gabrielse *et al.*, Driven production of cold antihydrogen and the first measured distribution of antihydrogen states, *Phys. Rev. Lett.* **89**, 233401 (2002).
 - [6] W. A. Bertsche, E. Butler, M. Charlton, and N. Madsen, Physics with antihydrogen, *J. Phys. B: At. Mol. Opt. Phys.* **48**, 232001 (2015).
 - [7] P. Pérez *et al.*, The GBAR antimatter gravity experiment, *Hyperfine Interact.* **233**, 21 (2015).
 - [8] M. Ahmadi *et al.*, Characterization of the 1S-2S transition in antihydrogen, *Nature (London)* **557**, 71 (2018).
 - [9] E. K. Anderson *et al.*, Observation of the effect of gravity on the motion of antimatter, *Nature (London)* **621**, 716 (2023).
 - [10] C. J. Baker *et al.*, Precision spectroscopy of the hyperfine components of the 1S–2S transition in antihydrogen, *Nat. Phys.* **21**, 201 (2025).
 - [11] W. Kolos, D. L. Morgan, D. M. Schrader, and L. Wolniewicz, Hydrogen-antihydrogen interactions, *Phys. Rev. A* **11**, 1792 (1975).
 - [12] D. L. Morgan and V. W. Hughes, Atom-antiatom interactions, *Phys. Rev. A* **7**, 1811 (1973).
 - [13] E. Fermi and E. Teller, The capture of negative mesotrons in matter, *Phys. Rev.* **72**, 399 (1947).
 - [14] D. K. Gridnev and C. Greiner, Proof that the hydrogen-antihydrogen molecule is unstable, *Phys. Rev. Lett.* **94**, 223402 (2005).
 - [15] A. Saenz, Density-matrix study of the hydrogen-antihydrogen molecule, *Z. Phys. C* **220**, 945 (2006).
 - [16] S. Jonsell, Rearrangement in antihydrogen-atom scattering, *Nucl. Instrum. Methods Phys. Res., Sect. B* **266**, 369 (2008).
 - [17] G. V. Shlyapnikov, J. T. M. Walraven, and E. L. Surkov, Antihydrogen at sub-Kelvin temperatures, *Hyperfine Interact.* **76**, 31 (1993).
 - [18] D. G. Fried, T. C. Killian, L. Willmann, D. Landhuis, S. C. Moss, D. Kleppner, and T. J. Greytak, Bose-Einstein condensation of atomic hydrogen, *Phys. Rev. Lett.* **81**, 3811 (1998).
 - [19] A. Y. Voronin and J. Carbonell, Antiproton–hydrogen annihilation at subkelvin temperatures, *Phys. Rev. A* **57**, 4335 (1998).
 - [20] P. Froelich, S. Jonsell, A. Saenz, B. Zygelman, and A. Dalgarno, Hydrogen-antihydrogen collisions, *Phys. Rev. Lett.* **84**, 4577 (2000).
 - [21] P. K. Sinha and A. S. Ghosh, Hydrogen anti-hydrogen elastic scattering using fully quantal method, *Europhys. Lett.* **49**, 558 (2000).
 - [22] S. Jonsell, A. Saenz, P. Froelich, B. Zygelman, and A. Dalgarno, Stability of hydrogen–antihydrogen mixtures at low energies, *Phys. Rev. A* **64**, 052712 (2001).
 - [23] E. A. G. Armour and C. W. Chamberlain, Calculation of cross sections for very low-energy hydrogen–antihydrogen scattering using the Kohn variational method, *J. Phys. B: At. Mol. Opt. Phys.* **35**, L489 (2002).
 - [24] P. Froelich, S. Jonsell, A. Saenz, S. Eriksson, B. Zygelman, and A. Dalgarno, Leptonic annihilation in hydrogen-antihydrogen collisions, *Phys. Rev. A* **70**, 022509 (2004).
 - [25] S. Jonsell, A. Saenz, P. Froelich, B. Zygelman, and A. Dalgarno, Hydrogen–antihydrogen scattering in the Born-Oppenheimer approximation, *J. Phys. B: At. Mol. Opt. Phys.* **37**, 1195 (2004).
 - [26] B. Zygelman, A. Saenz, P. Froelich, and S. Jonsell, Cold collisions of atomic hydrogen with antihydrogen atoms: An optical potential approach, *Phys. Rev. A* **69**, 042715 (2004).
 - [27] E. A. G. Armour, Y. Liu, and A. Vigier, Inclusion of the strong interaction in low-energy hydrogen–antihydrogen scattering using a complex potential, *J. Phys. B: At. Mol. Opt. Phys.* **38**, L47 (2005).
 - [28] S. Jonsell, A. Saenz, P. Froelich, B. Zygelman, and A. Dalgarno, Including the strong nuclear force in antihydrogen-scattering calculations, *Can. J. Phys.* **83**, 435 (2005).
 - [29] J. A. Cohen, Reactive collisions of atomic antihydrogen with H, He^+ and He, *J. Phys. B: At. Mol. Opt. Phys.* **39**, 1517 (2006).
 - [30] S. Jonsell, Low-temperature antihydrogen-atom scattering, *Nucl. Instrum. Methods Phys. Res. Sect. B* **247**, 138 (2006).
 - [31] S. Jonsell, Collisions involving antiprotons and antihydrogen: An overview, *Philos. Trans. R. Soc. A* **376**, 20170271 (2018).
 - [32] B. Zygelman, A. Saenz, P. Froelich, S. Jonsell, and A. Dalgarno, Radiative association of atomic hydrogen with antihydrogen at subkelvin temperatures, *Phys. Rev. A* **63**, 052722 (2001).
 - [33] K. Strasburger, Accurate Born-Oppenheimer potential energy curve for the hydrogen-antihydrogen system, *J. Phys. B: At. Mol. Opt. Phys.* **35**, L435 (2002).
 - [34] K. Strasburger, Hydrogen-antihydrogen interaction: Spectacular breakdown of the adiabatic approximation, *J. Phys. B: At. Mol. Opt. Phys.* **37**, 4483 (2004).
 - [35] P. K. Sinha and A. S. Ghosh, Capture cross sections at low energies for $\text{H}-\bar{\text{H}}$ scattering, *J. Phys. B: At. Mol. Opt. Phys.* **35**, L281 (2002).
 - [36] H. Stegeby, K. Piszczatowski, H. O. Karlsson, R. Lindh, and P. Froelich, Variational calculations for the hydrogen–antihydrogen system with a mass-scaled Born-Oppenheimer potential, *Centr. Eur. J. Phys.* **10**, 1038 (2012).

- [37] E. A. G. Armour and S. Jonsell, On the evaluation of transition matrices for rearrangement in atom–antiatom scattering, *J. Phys. A: Math. Theor.* **40**, 701 (2007).
- [38] A. Y. Voronin and P. Froelich, Resonant phenomena in antihydrogen-hydrogen scattering, *Phys. Rev. A* **77**, 022505 (2008).
- [39] K. Piszczatowski, A. Voronin, and P. Froelich, Nonadiabatic treatment of hydrogen-antihydrogen collisions, *Phys. Rev. A* **89**, 062703 (2014).
- [40] K. Piszczatowski, A. Voronin, and P. Froelich, Four-body calculations of elastic scattering in H– $\bar{\text{H}}$ collisions, *Hyperfine Interact.* **228**, 85 (2014).
- [41] H. Stegeby and K. Piszczatowski, Resonance states in the hydrogen–antihydrogen system from a nonadiabatic treatment, *J. Phys. B: At. Mol. Opt. Phys.* **49**, 014002 (2016).
- [42] T. Yamashita and Y. Kino, Coupled channel study of antihydrogen-hydrogen molecular resonance state, *JJAP Conf. Proc.* **7**, 011004 (2018).
- [43] E. Hiyama, Y. Kino, and M. Kamimura, Gaussian expansion method for few-body systems, *Prog. Part. Nucl. Phys.* **51**, 223 (2003).
- [44] L. Labzowsky, V. Sharipov, A. Prozorov, G. Plunien, and G. Soff, Decay channels and decay rates for the hydrogen-antihydrogen quasimolecule, *Phys. Rev. A* **72**, 022513 (2005).
- [45] A. Ferrón, P. Serra, and S. Kais, Stability conditions for hydrogen-antihydrogen-like quasimolecules, *Phys. Rev. A* **77**, 052505 (2008).
- [46] V. Sharipov, L. Labzowsky, and G. Plunien, Potential energy curves for excited states of the hydrogen–antihydrogen system, *Phys. Rev. Lett.* **97**, 103005 (2006).
- [47] V. Sharipov, L. Labzowsky, and G. Plunien, Rydberg states of the hydrogen-antihydrogen quasimolecule, *Phys. Rev. A* **73**, 052503 (2006).
- [48] K. Pachucki, M. Zientkiewicz, and V. Yerokhin, H2SOLV: Fortran solver for diatomic molecules in explicitly correlated exponential basis, *Comput. Phys. Commun.* **208**, 162 (2016).
- [49] The definition of the base parameters of Pachucki *et al.*, differs slightly from the original one introduced by Kołos and Wolniewicz, who used the symbols $\{\alpha, \bar{\alpha}, \beta, \bar{\beta}\}$. They are related by $uR = \alpha$, $wR = \bar{\alpha}$, $yR = -\beta$, and $xR = -\bar{\beta}$. The motivation for dividing the Kołos-Wolniewicz parameters by R is that in this case the exponential damping becomes independent of the interhadronic separation, since the implicit dependence contained in the prolate-spheroidal coordinates ξ and η is canceled.
- [50] D. H. Bailey, MPFUN2015: A thread-safe arbitrary precision package, <https://www.davidhbailey.com/dhsoftware/>.
- [51] Convergence plots for additional R values and also for the ten lowest-lying Q -odd states are given in Appendix B.
- [52] An alternative, still simplified diabatization technique would be to use the leading coefficients of the wave functions as a criterion for preserving the character of a state across an avoided crossing. This usually requires a very fine R grid for becoming (asymptotically) exact and is increasingly challenging in the case of a high density of states, like the one encountered here.
- [53] L. Wolniewicz, Relativistic energies of the ground state of the hydrogen molecule, *J. Chem. Phys.* **99**, 1851 (1993).
- [54] G. Staszewska and L. Wolniewicz, Transition moments among $^3\Sigma$ and $^3\Pi$ states of the H_2 molecule, *J. Mol. Spectrosc.* **198**, 416 (1999).
- [55] G. Staszewska and L. Wolniewicz, Adiabatic energies of excited $^1\Sigma_u$ states of the hydrogen molecule, *J. Mol. Spectrosc.* **212**, 208 (2002).
- [56] States with $\Lambda > 0$ can be calculated by constructing linear combinations which are symmetry adapted to $\hat{Q}\hat{\chi}$, where $\hat{\chi}$ is an irreducible representation of $\text{SO}(2)$. A more detailed discussion can, e.g., be found in Ref. [58], where H2SOLV was extended and used to compute Π , Δ , and Φ states of the hydrogen molecule.
- [57] S. Bubín and L. Adamowicz, Computer program ATOM-MOL-nonBO for performing calculations of ground and excited states of atoms and molecules without assuming the Born–Oppenheimer approximation using all-particle complex explicitly correlated Gaussian functions, *J. Chem. Phys.* **152**, 204102 (2020).
- [58] M. Siłkowski and K. Pachucki, Born–Oppenheimer potentials for Π , Δ , and Φ states of the hydrogen molecule, *Mol. Phys.* **120**, e2062471 (2022).