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Treatment of resonances in the scattering of a heavy positron by H_2 that are due to interaction with vibrationally excited quasibound states

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For a positron with wave number k, the rate of annihilation when scattered by an atom or molecule is proportional to $Z_{\text{eff}}(k)$, the effective number of electrons in the target that are available to the positron for annihilation. There is currently great interest in the very large positron annihilation rates, and hence values of $Z_{\text{eff}}(k)$, that have been observed in low-energy positron scattering by some molecules. These are observed experimentally to occur at energies just below the energies of excited vibrational states of the molecule concerned. This has been explained by Gribakin [Phys. Rev. A **61**, 022720 (2000)] and Gribakin and Lee [Phys. Rev. Lett. **97**, 193201 (2006)] as being due to Feshbach resonances involving excited quasibound vibrational states. These treatments make skilful use of approximate methods. It is of interest to determine how the expression obtained for the resonant contribution to $Z_{\text{eff}}(k)$ from a quasibound state using a very accurate method is related to the expressions obtained in the previously mentioned articles. In view of this, in this article I carry out a detailed *ab initio* theoretical treatment of positron scattering by H_2 using the Kohn variational method. H_2 is the simplest molecule, which makes it easier to take into account all the interactions involved. However, a positron does not form a bound state with H_2. To investigate resonant behavior in $Z_{\text{eff}}(k)$, I increase the mass m_p of the positron so that it forms a weakly bound state with H_2. This gives rise to excited quasibound vibrational states. The expression I obtain for the resonant contribution to $Z_{\text{eff}}(k)$ has some similarity with the expressions obtained by Gribakin and Lee. This gives some support to their explanation of the very large values of $Z_{\text{eff}}(k)$. However, they make no explicit mention of corrections to the Born-Oppenheimer (BO) approximation. These play a key role in my treatment as they couple the quasibound states to the continuum. I am able to show how the BO corrections are taken into account implicitly in calculating the expressions obtained by Gribakin and Lee. The most important difference between my treatment and their treatments is that in my treatment $Z_{\text{eff}}(k)$ may be infinite at the resonant energy, whereas in the other treatments it is likely to be large, but can never be infinite. Further investigation is necessary to determine the origin of this infinity in my treatment. My treatment could be applied to positron scattering by molecules such as methyl halides in which very high $Z_{\text{eff}}(k)$ values are observed, though using the Kohn variational method would be considerably more complicated than in the case of H_2.

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I. INTRODUCTION

One of the interesting processes that can take place when a positron is scattered by an atom or a molecule is positron annihilation. The positron annihilation rate, λ, for an incident positron with wave number, k, is given by

$$\lambda = \pi r_0^2 c D Z_{\text{eff}}(k), \tag{1}$$

where r_0 is the classical radius of the electron, D is the density of target atoms or molecules in the vicinity of the positron, and $Z_{\text{eff}}(k)$ is the effective number of electrons in the target that are available to the positron for annihilation.

There is currently great interest in the very large positron annihilation rates, and hence values of $Z_{\text{eff}}(k)$, that have been observed in low-energy positron scattering by some molecules. These are observed experimentally to occur just below excited vibrational states of the molecule concerned [1]. This has been explained by Gribakin and Lee [2,3] to be due to Feshbach resonances involving excited quasibound vibrational states.

Gribakin [2] calculates a scattering wave function made up of a component that describes the scattering of a positron by a molecule in its ground state and a second component that describes positron capture into quasibound positron-molecule states. From this he goes on to obtain expressions for the contributions to $Z_{\text{eff}}(k)$ from a resonant quasibound state and from the nonresonant part of the scattering wave function.

In a later article, Gribakin and Lee [3] use the Breit-Wigner formula directly to calculate $Z_{\text{eff}}(k)$ in the vicinity of a resonance and make approximations based on the assumption that the quasibound vibrational state involved is very diffuse. With suitable choice of the energy of the quasibound state, the Gribakin and Lee method gives good agreement for the very large observed $Z_{\text{eff}}(k)$ values obtained for positron scattering by, for example, CH_3F, CH_3Cl, and CH_3Br.

The treatments in [2] and [3] make skilful use of approximate methods. This entails using the Born-Oppenheimer (BO) approximation without any explicit investigation of the effects of including corrections to this approximation. It is of interest to determine how the expression obtained for the resonant contribution to $Z_{\text{eff}}(k)$ from a quasibound state using a very accurate method is related to the expressions obtained in [2] and [3].

In view of this, in this article I carry out a detailed *ab initio* treatment of positron scattering by the hydrogen molecule (H_2) using the Kohn variational method. H_2 is the simplest molecule, which makes it easier to take into account all the interactions involved. However, a positron does not form a bound state with H_2. To investigate resonant behavior in $Z_{\text{eff}}(k)$, I increase the mass m_p of the positron so that it forms

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a weakly bound state with H_2. I find that, as a consequence of this, there are quasibound vibrational states within the continuum that are eigenfunctions of the Hamiltonian for the system within the BO approximation. These states give rise to Feshbach resonances.

I find some agreement with the results obtained in [2] and [3]. This gives some support to their explanation of the very large values of $Z_{\text{eff}}(k)$. In my treatment, I take the corrections to the BO approximation explicitly into account. They play a key role in coupling the quasibound vibrational states to the continuum. I am able to show that these corrections are taken into account implicitly in [2] and [3].

The most important difference between my treatment and the treatments in [2] and [3] is that $Z_{\text{eff}}(k)$ may be infinite at the resonant energy in my treatment, whereas in the other treatments it is likely to be large, but can never be infinite.

I have carried out my treatment for a very simple system, namely, positron-H_2 with the positron mass increased so that a weakly bound positron-H_2 state is formed. However, the principles involved are the same if my treatment is applied to a molecule that can bind a positron. The main difference is the increase in complexity.

II. INVESTIGATION OF QUASIBOUND STATES

The system to be considered is a positron of mass m_p and an H_2 molecule. The units are hartree atomic units.

The nonrelativistic Hamiltonian, $\hat{H}$, for this system with respect to an inertial frame, is

$$\begin{aligned}\hat{H} = & -\frac{1}{2M}\nabla^2_{\mathbf{R}_A} - \frac{1}{2M}\nabla^2_{\mathbf{R}_B} - \frac{1}{2m_p}\nabla^2_1 - \frac{1}{2}\nabla^2_2 \\ & -\frac{1}{2}\nabla^2_3 + \frac{1}{r_{A1}} + \frac{1}{r_{B1}} - \frac{1}{r_{A2}} - \frac{1}{r_{B2}} - \frac{1}{r_{A3}} \\ & -\frac{1}{r_{B3}} + \frac{1}{R} - \frac{1}{r_{12}} - \frac{1}{r_{13}} + \frac{1}{r_{23}},\end{aligned} \tag{2}$$

where A and B are the nuclei; particle 1 is the positron and particles 2 and 3 are the electrons; $\mathbf{R}_A$ and $\mathbf{R}_B$ are the position vectors of nuclei A and B, respectively; $\mathbf{r}_i$ is the position vector of particle i; r_{ij} is the distance between particles i and j; $\mathbf{R}$ is the position vector of nucleus B with respect to nucleus A; and M is the mass of the proton.

It is of interest to investigate what kind of solutions we obtain for the Schrödinger equation for this system if we make the BO approximation. The Hamiltonian, $\hat{H}_{\text{lep}}$, for the leptons is

$$\begin{aligned}\hat{H}_{\text{lep}} = & -\frac{1}{2m_p}\nabla^2_1 - \frac{1}{2}\nabla^2_2 - \frac{1}{2}\nabla^2_3 + \frac{1}{r_{A1}} + \frac{1}{r_{B1}} - \frac{1}{r_{A2}} - \frac{1}{r_{B2}} \\ & - \frac{1}{r_{A3}} - \frac{1}{r_{B3}} - \frac{1}{r_{12}} - \frac{1}{r_{13}} + \frac{1}{r_{23}} + \frac{1}{R}.\end{aligned} \tag{3}$$

The coordinates are with respect to molecule-fixed axes with origin midway between the nuclei and the z axis along the internuclear axis from A to B. The nuclei are taken to be fixed. For details of the relationship between molecule-fixed coordinates and nonrotating coordinates, see, for example, Armour and Jonsell [4].

The Schrödinger equation for the leptons with the nuclei fixed is

$$\hat{H}_{\text{lep}}\Psi_{\text{lep},m}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3;\mathbf{R}) = E_m(R)\Psi_{\text{lep},m}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3;\mathbf{R}). \tag{4}$$

We can adjust the value of m_p of the positron so that the leptons have a weakly bound state. It is to be expected that as m_p is increased a bound state will first appear at $R \approx 3.4a_0$, as Zhang *et al.* [5] have recently shown that there is a virtual state at this R value. This is far into the classically forbidden region for the ground vibrational state. I assume, at this stage, that m_p is adjusted so that a weakly bound state exists for all R values for which the associated vibrational wave function differs appreciably from zero. Note that the range of R values for which this condition is assumed to be satisfied increases with the energy associated with the vibrational wave function.

In principle, we can solve (4) exactly to obtain both the bound-state wave function corresponding to all such R values and also a continuum wave function corresponding to a positron with incident energy E_p. In the case of the weakly bound state, $E_m(R)$ will have a value slightly below the value, $E_{\text{mol}}(R)$, that would be obtained if the positron were not in the system. In the case of the continuum state,

$$E_m(R) = E_{\text{mol}}(R) + E_p \quad \forall R. \tag{5}$$

Approximations to wave functions for such states have been calculated with $m_p = 1$ for a given R value, in most cases the H_2 equilibrium value, $1.4a_0$, using the Kohn variational method [6,7].

If we proceed to the next stage of the BO approximation, we take the wave function for the system, including the nuclei, to be $\Psi_{\text{lep},m}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3;\mathbf{R})\chi_{mn}(\mathbf{R})$, where $\chi_{mn}(\mathbf{R})$ is a vibrational-rotational wave function.

If we separate out the center-of-mass motion, neglecting the reduced mass and mass polarization corrections to the kinetic energy of the leptons that result from the fact that the nuclei do not have infinite mass, the Schrödinger equation for the internal motion of the system has the form

$$\left(-\frac{1}{2\mu_M}\nabla^2_{\mathbf{R}} + \hat{H}_{\text{lep}}\right)\Psi = E\Psi, \tag{6}$$

where μ_M is the reduced mass of the nuclei. If we let $\Psi = \Psi_{\text{lep},m}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3;\mathbf{R})\chi_{mn}(\mathbf{R})$, this becomes

$$\left(-\frac{1}{2\mu_M}\nabla^2_{\mathbf{R}} + \hat{H}_{\text{lep}}\right)\Psi_{\text{lep},m}\chi_{mn} = E\Psi_{\text{lep},m}\chi_{mn}. \tag{7}$$

The lepton coordinates to be kept fixed when carrying out the partial differentiations in $\nabla^2_{\mathbf{R}}$ are coordinates with respect to nonrotating axes with origin at the center of mass of the nuclei. The leptonic coordinates used in $\Psi_{\text{lep},m}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3;\mathbf{R})$ are taken to have the same origin, but they are with respect to molecule-fixed axes with z axis along the internuclear axis from A to B. For a given lepton, the two sets of coordinates are related by a proper, orthogonal transformation involving the spherical polar angles of $\mathbf{R}$ with respect to the nonrotating axes.

If this change of constant variables in the partial differentiations in $\nabla^2_{\mathbf{R}}$ is taken into account using the chain rule, centrifugal and Coriolis terms involving the leptonic coordinates are obtained in addition to $\nabla^2_{\mathbf{R}}$ with the molecule-fixed coordinates kept constant in the partial differentiation [4].

Note that only the centrifugal and Coriolis terms that operate solely on the leptonic coordinates will be nonzero if the nuclei are in their ground rotational state. Note also that if an R dependence is introduced into the leptonic coordinates, additional terms result as a consequence of this dependence. This is the case, if, for example, prolate spheroidal coordinates are used [6,7]. These terms represent coupling between the vibrational motion of the nuclei and the motion of the leptons.

In the BO approximation, the preceding centrifugal, Coriolis, and vibrational coupling terms are neglected and (7) takes the form

$$-\frac{1}{2\mu_M}\left(\nabla^2_{\mathbf{R}}\Psi_{\text{lep},m}\right)\chi_{mn}-\frac{1}{\mu_M}(\nabla_{\mathbf{R}}\Psi_{\text{lep},m}\cdot\nabla_{\mathbf{R}}\chi_{mn}) -\frac{1}{2\mu_M}\Psi_{\text{lep},m}\nabla^2_{\mathbf{R}}\chi_{mn}+E_m(R)\Psi_{\text{lep},m}\chi_{mn}=E_{mn}\Psi_{\text{lep},m}\chi_{mn}, \tag{8}$$

where in the partial differentiations with respect to the coordinates of $\mathbf{R}$, the molecule-fixed coordinates are kept constant.

In the BO approximation, the further step is taken of neglecting the terms involving $\nabla^2_{\mathbf{R}}\Psi_{\text{lep},m}$ and $\nabla_{\mathbf{R}}\Psi_{\text{lep},m}$ as they are much smaller than the term involving $\nabla^2_{\mathbf{R}}\chi_{mn}$ for values of R close to the equilibrium value for H_2, which is $1.4a_0$. See, for example, Bransden and Joachain [8].

If we divide both sides of the resulting equation by $\Psi_{\text{lep},m}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3;\mathbf{R})$, we obtain

$$-\frac{1}{2\mu_M}\nabla^2_{\mathbf{R}}\chi_{mn}+E_m(R)\chi_{mn}=E_{mn}\chi_{mn}. \tag{9}$$

I denote the bound state by $m=0$. Its energy $E_0(R)$ gives rise to a nuclear potential that is slightly more attractive than $E_{\text{mol}}(R)$, the nuclear potential for the H_2 molecule in the absence of the positron. Thus, if we are considering the ground vibrational state, which I denote by $n=0$, E_{00} will be slightly below the energy of H_2+ the positron at rest at infinity. Thus, in the BO approximation this will correspond to a bound state. This can be seen from the fact that $\Psi_{\text{lep},0}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3;\mathbf{R})\chi_{00}(\mathbf{R})$ satisfies the Schrödinger equation (5) with E_{00} as described if the BO approximation is made in evaluating

$$-\frac{1}{2\mu_M}\nabla^2_{\mathbf{R}}\Psi_{\text{lep},0}\chi_{00}.$$

However, the states $\{\Psi_{\text{lep},0}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3;\mathbf{R})\chi_{0n}(\mathbf{R})\}$ $(n>0)$ also satisfy the Schrödinger equation (6) in this approximation. These will have energies E_{0n} $(n>0)$ that are in the continuum corresponding to continuum states with energy E_{10}, where $m=1$ denotes a continuum state. The states $\{\Psi_{\text{lep},0}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3;\mathbf{R})\chi_{0n}(\mathbf{R})\}$ $(n>0)$ are bound lepton states but with associated vibrational states $\{\chi_{0n}(\mathbf{R})\}$ $(n>0)$ other than the ground state. They will be slightly lower in energy than the corresponding ground electronic, vibrational states of the target.

These states can have a range of values of the total angular momentum. For simplicity, I only consider those for which this is zero.

The states do not couple to the continuum in the BO approximation. However, if we go beyond the BO approximation, such states couple to the continuum and become quasibound. It is to be expected that this coupling will bring about resonances in positron-H_2 scattering for incident positron energies, E_p, such that

$$E_p+E_{\text{target}}\approx E_{0n}. \tag{10}$$

III. INVESTIGATION OF RESONANCES USING THE KOHN METHOD

I investigate the effect of such resonances on $Z_{\text{eff}}(k)$ using the Kohn variational method. To do this I take the Hamiltonian to be in the center-of-mass frame; that is,

$$\hat{H}_{\text{c.m.}}=-\frac{1}{2\mu_M}\nabla^2_{\mathbf{R}}+\hat{H}_{\text{lep}}. \tag{11}$$

I have neglected the reduced mass and mass polarization corrections to the kinetic energy of the leptons as this is the usual practice in calculations of both atomic and molecular scattering (see, for example, [9]). The reduced mass corrections would be easy to include but including the mass polarization corrections would be more complicated. All other corrections to the BO approximation are included.

I assume that the lowest quasibound state corresponding to $n=0$ remains bound when the BO corrections are included. Note that this state will be just below the energy of the system when the incident positron energy is zero and will thus give rise to a resonance at this energy. I assume that there are N_r higher-energy quasibound states corresponding to $n=1,2,\ldots,N_r$.

It is convenient to adjust the labeling of the quasibound states so that the quasibound state whose resonant properties are to be investigated has $n=1$. This can be done without loss of generality. For simplicity, I take this quasibound state to be the lowest in energy.

In order to highlight the role of the quasibound states in bringing about resonant behavior, it is convenient in the Kohn calculation to split the Hilbert space, Λ, of possible basis functions up into two disjoint subspaces, Γ and $\Gamma^{\perp}$. Γ has as basis the N_r orthonormal quasibound states $\{\Psi_{\text{lep},0}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3;\mathbf{R})\chi_{0i}(R)\}_{i=1}^{N_r}$, where the common leptonic part of the wave function is taken to be normalized for all values of $\mathbf{R}$.

$\Gamma^{\perp}$ is the subspace of all possible basis functions that are orthogonal to the N_r quasibound states. This is to be thought of as including continuum functions, though strictly speaking they are not contained in Λ. The projection operators $\hat{P}_{\Gamma^{\perp}}$ and $\hat{P}_{\Gamma}$, associated with $\Gamma^{\perp}$ and Γ, respectively, are similar to the projection operators $\hat{P}$ and $\hat{Q}$ in the case of Feshbach's treatment of isolated resonances in nuclear reactions [10]. The role of projection operators in calculations on electron-molecule scattering is considered by Domcke [11].

The Kohn trial function, $\Psi_{\text{trial}}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\mathbf{R};k)$, is taken to be of the form

$$\begin{aligned}\Psi_{\text{trial}}&(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\mathbf{R};k)\\ &=\Psi_{0a}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\mathbf{R};k)+a_{11}\Psi_{0b}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\mathbf{R};k)\\ &\quad+a_{21}\Psi_{0c}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\mathbf{R};k)+\sum_{i=1}^{N}c_i\phi_i(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\mathbf{R})\\ &\quad+\sum_{i=1}^{N_r}d_i\Psi_{\text{lep},0}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3;\mathbf{R})\chi_{0i}(R),\end{aligned} \tag{12}$$

where

$$\Psi_{0a}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\mathbf{R};k) \sim_{r_1\to\infty} \Psi_{\text{target}}(\mathbf{r}_2,\mathbf{r}_3,\mathbf{R})\frac{1}{\sqrt{4\pi}}\frac{\sin kr_1}{kr_1}, \tag{13}$$

$$\Psi_{0b}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\mathbf{R};k) \sim_{r_1\to\infty} \Psi_{\text{target}}(\mathbf{r}_2,\mathbf{r}_3,\mathbf{R})\frac{1}{\sqrt{4\pi}}\frac{\cos kr_1}{kr_1}, \tag{14}$$

$$\Psi_{0c}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\mathbf{R};k) \sim_{r_1\to\infty} \Psi_{\text{target}}(\mathbf{r}_2,\mathbf{r}_3,\mathbf{R})\sqrt{\frac{5}{4\pi}}\frac{\cos(kr_1-\pi)}{kr_1}P_2(\cos\bar{\theta}_1), \tag{15}$$

and $\Psi_{\text{target}}(\mathbf{r}_2,\mathbf{r}_3,\mathbf{R})$ is the normalized target wave function.

All the basis functions in $\Psi_{\text{trial}}(k)$ are taken to be real. In addition, all of them, except the N_r quasibound states, are taken to be in $\Gamma^{\perp}$ and the short-range correlation functions $\{\phi_i\}_{i=1}^{N}$ are taken to be orthonormal. It is assumed that the trial function can fit the exact scattering wave function very accurately. $\mathbf{k}$ is the momentum of the incident positron which is taken to be in the z direction with respect to the nonrotating axes. $\Psi_{\text{target}}(\mathbf{r}_2,\mathbf{r}_3,\mathbf{R})$ is the ground-state electronic and vibrational-rotational target H_2 wave function. The spin wave function is a singlet. As the Hamiltonian $\hat{H}_{\text{c.m.}}$ does not involve spin, this wave function can be omitted. However, to satisfy the Pauli exclusion principle, the ground-state wave function and the scattering wave function must be symmetric with respect to interchange of the electrons. The origin of the coordinates of the positron, particle 1, is taken to be at the center of mass of the nuclei. The polar angle $\bar{\theta}_1$ is with respect to the molecule-fixed coordinates which are free to rotate. It would be possible to use continuum functions expressed in terms of prolate spheroidal coordinates, as in [6,7]. However, they are more complicated and, as pointed out earlier, introduce coupling with the vibrational motion of the nuclei.

The continuum function containing $P_2(\cos\bar{\theta}_1)$ represents mixing of partial waves in the molecule-fixed frame. Such mixing tends to zero as k tends to zero, but increases as k increases. The extent of mixing is very small at the k values I consider. If necessary at higher energies, continuum functions containing higher Legendre polynomials with even index could be included in the trial function. Those with an odd index are excluded by the gerade symmetry of the partial wave with zero angular momentum.

Inclusion of continuum functions containing $P_l(\cos\bar{\theta}_1)$, where $l = 2,4,\ldots,$ does not violate conservation of angular momentum as

$$P_l(\cos\bar{\theta}_1) = \frac{4\pi}{2l+1}\sum_m Y_{lm}(\theta_1,\phi_1)Y_{lm}^*(\theta,\phi), \tag{16}$$

where Y_{lm} is a spherical harmonic, θ_1 and ϕ_1 are the spherical polar angles of the positron with respect to the nonrotating coordinates, and θ and ϕ are the corresponding angles of $\mathbf{R}$. For a given l value, the right-hand side of (16) corresponds to the combination, in the nonrotating frame, of positron and nuclear states, each of angular momentum l, that is a scalar and thus has zero overall angular momentum (see, for example, [12]).

To set up the equations of the Kohn variational method that determine the coefficients $\{a_{11},a_{21},c_1,\ldots,c_N,d_{N_r},\ldots,d_1\}$ in the trial function for a scattering state of energy $E = E_p + E_{\text{target}}$, we must calculate matrix elements of $\hat{H}_{\text{c.m.}} - E$ between the basis functions in the trial function (see, for example, [9]). The Kohn equations are of the form

$$Ax = -b, \tag{17}$$

where A is the matrix representation of $\hat{F} = \hat{H}_{\text{c.m.}} - E$ over the basis functions Ψ_{0b}, Ψ_{0c}, $\phi_1,\ldots,\phi_N$, $\Psi_{\text{lep},0}\chi_{0N_r},\ldots,$ $\Psi_{\text{lep},0}\chi_{01}$, labeled in that order, as this is advantageous for proving the results obtained:

$$x = [a_{11}a_{21}c_1\cdots c_N d_{N_r}\cdots d_1]^{\top} \tag{18}$$

and

$$b = \big[\langle\Psi_{0b}|\hat{F}|\Psi_{0a}\rangle\langle\Psi_{0c}|\hat{F}|\Psi_{0a}\rangle\langle\phi_1|\hat{F}|\Psi_{0a}\rangle\cdots\langle\phi_N|\hat{F}|\Psi_{0a}\rangle \times\big\langle\Psi_{\text{lep},0}\chi_{0N_r}\big|\hat{F}|\Psi_{0a}\big\rangle\cdots\langle\Psi_{\text{lep},0}\chi_{01}|\hat{F}|\Psi_{0a}\rangle\big]^{\top}. \tag{19}$$

Note that as $\hat{F}$ is Hermitian and all the basis functions are real, A is a real, symmetric matrix. This property is unaffected by the inclusion of two continuum functions in A.

If $\hat{H}_{\text{c.m.}} - E$ operates on a quasibound state, we obtain

$$(\hat{H}_{\text{c.m.}} - E)|\Psi_{\text{lep},0}\chi_{0i}\rangle = (E_{0i} - E)|\Psi_{\text{lep},0}\chi_{oi}\rangle + \frac{1}{\mu_M}|\zeta_i\rangle + \frac{1}{\mu_M}|\omega_i\rangle \; i \in (1,2,\ldots,N_r), \tag{20}$$

where $|\zeta_i\rangle\epsilon\Gamma^{\perp}$ and $|\omega_i\rangle\epsilon\Gamma$. These kets result from the operation on $\{\Psi_{\text{lep},0}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3;\mathbf{R})\chi_{0i}(R)\}$ of the terms in $\hat{H}_{\text{c.m.}}$ that represent corrections to the BO approximation. Such terms are all proportional to $1/\mu_M$, where μ_M is the reduced mass of the nuclei. To draw attention to this, I have inserted a factor of $1/\mu_M$ in front of these kets on the right-hand side of (20).

Using the Hermiticity of $\hat{F}$ and the properties of the kets $\{|\zeta_i\rangle\}$ and $\{|\omega_i\rangle\}$ $(i = 1,\ldots,N_r)$, matrix elements involving $\Psi_{\text{lep},0}\chi_{0i}$ and a basis function contained in $\Gamma^{\perp}$ reduce to a form containing ζ_i. Thus, in the case of ϕ_1, for example,

$$\langle\phi_1|\hat{F}|\Psi_{\text{lep},0}\chi_{0i}\rangle = \frac{1}{\mu_M}\langle\phi_1|\zeta_i\rangle. \tag{21}$$

In the case of a basis function contained in Γ, ζ_i on the right-hand side is replaced with ω_i.

The column vector b takes the form

$$b = \left[\langle\Psi_{0b}|\hat{F}|\Psi_{0a}\rangle\langle\Psi_{0c}|\hat{F}|\Psi_{0a}\rangle\langle\phi_1|\hat{F}|\Psi_{0a}\rangle\cdots\langle\phi_N|\hat{F}|\Psi_{0a}\rangle \times\frac{1}{\mu_M}\big\langle\zeta_{N_r}\big|\Psi_{0a}\big\rangle\cdots\frac{1}{\mu_M}\langle\zeta_1|\Psi_{0a}\rangle\right]^{\top}. \tag{22}$$

As stated earlier, the index of the quasibound states has been adjusted so that the state with $i = 1$ is the state whose resonant properties are to be investigated. The coefficient, d_1, of this state in the trial function, $\Psi_{\text{trial}}(k)$, can be calculated using Cramer's rule. Assuming that A is nonsingular,

$$d_1 = \frac{\det(A_{C,p})}{\det(A)} \qquad (p = N + N_r + 2), \tag{23}$$

where $A_{C,p}$ is the matrix obtained by replacing the $(N+N_r+2)$th, that is, the last, column of A with the column vector $-b$.

If we expand $\det(A_{C,p})$ and $\det(A)$ on the last column of each determinant, we obtain

$$d_1 = -\frac{\langle\Psi_{0b}|\hat{F}|\Psi_{0a}\rangle A'_{1p} + \cdots + \langle\Psi_{\text{lep},0}\chi_{01}|\hat{F}|\Psi_{0a}\rangle A'_{pp}}{\frac{1}{\mu_M}\langle\Psi_{0b}|\zeta_1\rangle A'_{1p} + \cdots + \big(E_{01} - E + \frac{1}{\mu_M}\langle\Psi_{\text{lep},0}\chi_{01}|\omega_1\rangle\big)A'_{pp}}, \tag{24}$$

where A'_{ip} is the cofactor of the element in the ith row and pth column of $\det(A)$.

Multiplying the numerator and denominator of the right-hand side of (24) by μ_M/A'_{pp}, we obtain

$$d_1 = -\frac{\mu_M(\langle\Psi_{nr}|\hat{F}|\Psi_{0a}\rangle + \langle\Psi_{\text{lep},0}\chi_{01}|\hat{F}|\Psi_{0a}\rangle)}{\langle\Psi_{nr}|\zeta_1+\omega_1\rangle + \mu_M\big(E_{01} - E + \frac{1}{\mu_M}\langle\Psi_{\text{lep},0}\chi_{01}|\omega_1\rangle\big)}, \tag{25}$$

where

$$\Psi_{nr} = g_1\Psi_{0b} + g_2\Psi_{0c} + \sum_{i=3}^{N+2} g_i\phi_i + \sum_{i=N+3}^{p-1} g_i\Psi_{\text{lep},0}\chi_{0j} \quad (j = i-N-1) \tag{26}$$

and

$$g_i = \frac{A'_{ip}}{A'_{pp}} \qquad (A'_{pp} \neq 0). \tag{27}$$

It is shown in the Appendix that the coefficients $\{g_i\}_{i=1}^{p-1}$ are such that $\langle\Psi_{nr} + \Psi_{\text{lep},0}\chi_{01}|\hat{H}_{\text{c.m.}} - E|\Psi_{nr} + \Psi_{lep,0}\chi_{01}\rangle$ is stationary for variations of these coefficients. This gives a physical interpretation to this wave function.

We can see that the denominator in the expression for d_1 in (25) is zero if

$$E = E_{01} + \frac{1}{\mu_M}(\langle\Psi_{\text{lep},0}\chi_{01}|\omega_1\rangle + \langle\Psi_{nr}|\zeta_1+\omega_1\rangle). \tag{28}$$

Ψ_{nr} depends on E. Thus, (28) is an equation for E. It is to be expected that the term containing Ψ_{nr} will be small in the vicinity of the resonance on account of the above stationary condition, as $\Psi_{\text{lep},0}\chi_{01}$ will almost be an eigenfunctionin this region. It is thus probable that there will be a value of E, E_{res}, not far from $E_{01} + \frac{1}{\mu_m}\langle\Psi_{\text{lep},0}\chi_{01}|\omega_1\rangle$ at which (28) is satisfied, making d_1 infinite. In any event, d_1 will be large when E is close to this value.

The second and third terms on the right-hand side of this equation are level shifts. The first of these terms represents the first-order contribution to the energy of the quasibound state with $i = 1$, due to the corrections to the BO approximation.

Note that it would be possible to include the corrections within Γ to all orders by diagonalizing the matrix representation of $\hat{H}_{\text{c.m.}}$ over the quasibound states, $\{\Psi_{\text{lep},0}\chi_{0i}\}_{i=1}^{N_r}$. The resulting quasibound states, $\{\Psi_{\text{lep},0}\Sigma_j f_{ij}\chi_{0j}\}_{i=1}^{N_r}$, where $\{f_{ij}\}$ are the coefficients determined by the diagonalization, are such that

$$(\hat{H}_{\text{c.m.}} - E)\left|\Psi_{\text{lep},0}\sum_{j=1}^{N_r} f_{ij}\chi_{0j}\right\rangle = (\bar{E}_{0i} - E)\left|\Psi_{\text{lep},0}\sum_{j=1}^{N_r} f_{ij}\chi_{0j}\right\rangle + \frac{1}{\mu_M}|\bar{\zeta}_i\rangle, \tag{29}$$

where $|\bar{\zeta}_i\rangle \in \Gamma^\perp$.

If the preceding analysis is repeated using the new quasibound states, terms corresponding to those in (24) that contain ω_i $(i = 1,\ldots,N_r)$ are zero and the corresponding coefficient, $\bar{d}_1$, is infinite when E satisfies the equation

$$E = \bar{E}_{01} + \frac{1}{\mu_M}(\langle\bar{\Psi}_{nr}|\bar{\zeta}_1\rangle), \tag{30}$$

where $\bar{E}_{01}$ contains the corrections to the BO approximation within Γ to all orders and $\bar{\Psi}_{nr}$ is similar to Ψ_{nr} but is evaluated using the new quasibound states.

IV. RESONANT BEHAVIOR OF $Z_{\text{eff}}(k)$

$Z_{\text{eff}}(k)$ can be obtained from the trial function, $\Psi_{\text{trial}}(k)$, by using the relation

$$Z_{\text{eff}}(k) = |B|^2\langle\Psi_{\text{trial}}(k)|\sum_{i=2}^{3}\delta(\mathbf{r}_1 - \mathbf{r}_i)|\Psi_{\text{trial}}(k)\rangle, \tag{31}$$

where $\delta(\mathbf{r}_1 - \mathbf{r}_i)$ is the Dirac δ function and B is a normalization constant such that the zero angular momentum partial wave has the appropriate coefficient for an incident positron beam with density of one particle per unit volume.

Thus, using (12) and the fact that $\Psi_{\text{trial}}(k)$ is real, $Z_{\text{eff}}(k)$ can be expressed in the form

$$\begin{aligned} Z_{\text{eff}} = |B|^2\Bigg[& d_1^2\langle\Psi_{\text{lep},0}\chi_{01}|\sum_{i=2}^{3}\delta(\mathbf{r}_1 - \mathbf{r}_i)|\Psi_{\text{lep},0}\chi_{01}\rangle \\ & + 2\,d_1\langle\Psi_{\text{trial},nr}(k)|\sum_{i=2}^{3}\delta(\mathbf{r}_1 - \mathbf{r}_i)|\Psi_{\text{lep},0}\chi_{01}\rangle \\ & + \Big\langle\Psi_{\text{trial},nr}(k)|\sum_{i=2}^{3}\delta(\mathbf{r}_1 - \mathbf{r}_i)|\Psi_{\text{trial},nr}(k)\Big\rangle\Bigg], \end{aligned} \tag{32}$$

where

$$\Psi_{\text{trial},nr}(k) = \Psi_{0a}(k) + a_{11}\Psi_{0b}(k) + a_{21}\Psi_{0c}(k) + \sum_{i=1}^{N} c_i\phi_i(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\mathbf{R}) + \sum_{i=2}^{N_r} d_i\Psi_{\text{lep},0}\chi_{0i}. \tag{33}$$

The first term on the right-hand side of (32) represents the contribution to $Z_{\mathrm{eff}}(k)$ purely from the resonant quasibound state $\Psi_{\mathrm{lep},0}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3;\mathbf{R})\chi_{01}(\mathbf{R})$.

We can obtain a useful approximate form for the factor d_1 in this term. The matrix elements in the numerator of Eq. (25) for d_1 are made up of elements of the form

$$\langle \eta|\hat{F}|\Psi_{0a}\rangle = \langle \eta|\hat{H}_{\mathrm{c.m.}} - E|\Psi_{0a}\rangle,$$

where η is a basis function in the trial function not equal to Ψ_{0a}. Ψ_{0a} would have the asymptotic form given in (13) for all r_1 if it were not for the requirement that $\Psi_{0a} \in \Gamma^{\perp}$; that is, it is orthogonal to all the quasibound states.

As the energy $E_m(R)$ associated with the weakly bound state is only slightly below $E_{\mathrm{mol}}(R)$, the value for the H_2 molecule, the vibrational wave functions of the quasibound states will not differ much from those of the H_2 molecule in its electronic ground state, calculated using the BO approximation. They will thus be approximately orthogonal to all the H_2 vibrational wave functions, except the one that has an energy just above the energy of the quasibound state under consideration.

The exact target wave function, $\Psi_{\mathrm{target}}(\mathbf{r}_2,\mathbf{r}_3,\mathbf{R})$, is made up of a superposition of H_2 BO states with the largest component, $\Psi_{\mathrm{target}}(\mathbf{r}_2,\mathbf{r}_3;\mathbf{R})\chi_0(R)$, where $\Psi_{\mathrm{target}}(\mathbf{r}_2,\mathbf{r}_3;\mathbf{R})$ is the target electronic wave function in the BO approximation and $\chi_0(R)$ is the associated ground-state vibrational wave function.

It follows from all this that

$$\begin{aligned}\Psi_{0a}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\mathbf{R}) &\approx \Psi_{\mathrm{target}}(\mathbf{r}_2,\mathbf{r}_3,\mathbf{R})\frac{1}{\sqrt{4\pi}}\frac{\sin kr_1}{kr_1}\\ &\approx \Psi_{\mathrm{target}}(\mathbf{r}_2,\mathbf{r}_3;\mathbf{R})\chi_0(R)\frac{1}{\sqrt{4\pi}}\frac{\sin kr_1}{kr_1}, \qquad (34)\end{aligned}$$

and hence that

$$\begin{aligned}&(\hat{H}_{\mathrm{c.m.}} - E)\Psi_{0a}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\mathbf{R})\\ &\quad\approx (\hat{H}_{\mathrm{c.m.}} - E)\Psi_{\mathrm{target}}(\mathbf{r}_2,\mathbf{r}_3,\mathbf{R})\frac{1}{\sqrt{4\pi}}\frac{\sin kr_1}{kr_1}\\ &\quad= V_p\Psi_{\mathrm{target}}(\mathbf{r}_2,\mathbf{r}_3,\mathbf{R})\frac{1}{\sqrt{4\pi}}\frac{\sin kr_1}{kr_1}, \qquad (35)\end{aligned}$$

where

$$V_p = \frac{1}{r_{A1}} + \frac{1}{r_{B1}} - \frac{1}{r_{12}} - \frac{1}{r_{13}} \qquad (36)$$

is the potential between the positron and the particles in H_2. We can deduce from this that

$$\langle \eta|\hat{F}|\Psi_{0a}\rangle \approx \langle \eta|V_p|\Psi_{0a}\rangle. \qquad (37)$$

Note that this relation holds even if

$$\eta = \Psi_{\mathrm{lep},0}\chi_{0i}, \qquad (38)$$

and in this case

$$\langle \eta|\hat{F}|\Psi_{0a}\rangle = \frac{1}{\mu_M}\langle \zeta_i|\Psi_{0a}\rangle, \qquad (39)$$

where $\frac{1}{\mu_M}\zeta_i$ is the component in $\Gamma^{\perp}$ resulting from the operation on $\Psi_{\mathrm{lep},0}\chi_{0i}$ of the terms in $\hat{H}_{\mathrm{c.m.}}$ that are corrections to the BO approximation.

It follows from the preceding that

$$d_1 \approx -\frac{\mu_M(\langle\Psi_{nr}|V_p|\Psi_{0a}\rangle + \langle\Psi_{\mathrm{lep},0}\chi_{01}|V_p|\Psi_{0a}\rangle)}{\langle\Psi_{nr}|\zeta_1+\omega_1\rangle + \mu_M\big(E_{01} - E + \frac{1}{\mu_M}\langle\Psi_{\mathrm{lep},0}\chi_{01}|\omega_1\rangle\big)}. \qquad (40)$$

At zero incident positron energy, $(E_{01} - E) \approx 0.019$ a.u. as the quasibound state with $n = 1$ has been chosen to be the lowest in energy. Also, the much larger masses of the nuclei as compared with the electrons make $\mu_M = 918$. The level shift term in $\frac{1}{\mu_M}$ in the coefficient of the term in μ_M can be neglected as it will be small in comparison with $(E_{01} - E)$. Thus, at zero incident energy,

$$\mu_M\left(E_{01} - E + \frac{1}{\mu_M}\langle\Psi_{\mathrm{lep},0}\chi_{01}|\omega_1\rangle\right) \approx 17.5. \qquad (41)$$

However, if $E = E_{\mathrm{res}}$ and thus satisfies (28), the denominators of (25) and (40) will be zero, making d_1 infinite. As can be seen from (32), the resonant contribution to $Z_{\mathrm{eff}}(k)$ contains d_1^2 as a factor. Thus, it will also be infinite at this E value.

We can obtain some information about the structure of the resonance from the dependence of the resonant contribution to $Z_{\mathrm{eff}}(k)$ on d_1^2. In [3], the width of the resonant contribution follows immediately from the Breit-Wigner formula. The situation in my treatment is more complicated as d_1^2 does not have this form. However, it follows from the form of the denominator in the expressions for d_1 in (25) and (40) that the resonant contribution will behave approximately as $(E_{\mathrm{res}} - E)^{-2}$ in the vicinity of the resonance. Equation (41) gives an indication how the denominator in (40) varies with energy in the region below the resonance.

The second term in (32) depends linearly on d_1 and thus will also be infinite when $E = E_{\mathrm{res}}$. However, the dominant infinity will be in the first term considered earlier as it is dependent on d_1^2. The second term represents contributions from the cross terms between $\Psi_{\mathrm{lep},0}\chi_{01}$ and the other functions in $\Psi_{\mathrm{trial}}(k)$. This can be seen if we expand the matrix element in this term as follows:

$$\begin{aligned}&\langle\Psi_{\mathrm{trial},nr}(k)|\sum_{i=2}^{3}\delta(\mathbf{r}_1 - \mathbf{r}_i)|\Psi_{\mathrm{lep},0}\chi_{01}\rangle\\ &\quad= \langle\Psi_{0a}(k)|\sum_{i=2}^{3}\delta(\mathbf{r}_1 - \mathbf{r}_i)|\Psi_{\mathrm{lep},0}\chi_{01}\rangle\\ &\qquad+ a_{11}\langle\Psi_{0b}(k)|\sum_{i=2}^{3}\delta(\mathbf{r}_1 - \mathbf{r}_i)|\Psi_{\mathrm{lep},0}\chi_{01}\rangle\\ &\qquad+ a_{21}\langle\Psi_{0c}(k)|\sum_{i=2}^{3}\delta(\mathbf{r}_1 - \mathbf{r}_i)|\Psi_{\mathrm{lep},0}\chi_{01}\rangle\\ &\qquad+ \sum_{j=1}^{N}c_j\langle\phi_j|\sum_{i=2}^{3}\delta(\mathbf{r}_1 - \mathbf{r}_i)|\Psi_{\mathrm{lep},0}\chi_{01}\rangle\\ &\qquad+ \sum_{j=2}^{N_r}d_j\langle\Psi_{\mathrm{lep},0}\chi_{0j}|\sum_{i=2}^{3}\delta(\mathbf{r}_1 - \mathbf{r}_i)|\Psi_{\mathrm{lep},0}\chi_{01}\rangle. \qquad (42)\end{aligned}$$

The δ function operates only on the leptonic coordinates. Thus, as

$$\langle \chi_{0i}(R)|\chi_{0j}(R)\rangle = \delta_{ij}, \tag{43}$$

the terms in (42) that involve only the quasibound states would all be zero if

$$Z_{\mathrm{eff,lep}}(R) = \langle \Psi_{\mathrm{lep},0}|\sum_{i=2}^{3}\delta(\mathbf{r}_1-\mathbf{r}_i)|\Psi_{\mathrm{lep},0}\rangle_{\mathbf{r}}, \tag{44}$$

where $\langle\;\rangle_{\mathbf{r}}$ denotes integration over the leptonic coordinates, were constant for all R values for which $\chi_{01}(R)$ differs appreciably from zero. Note that $Z_{\mathrm{eff,lep}}(R)$ is the value, for a given R, of $Z_{\mathrm{eff}}(k)$ calculated using the leptonic bound-state wave function.

The dominant vibrational component of Ψ_{0b},Ψ_{0c} and most of the short-range correlation functions $\{\phi_i\}_{i=1}^{N}$ will be χ_0, the H_2 ground-state vibrational wave function in the BO approximation. As χ_0 is almost orthogonal to χ_{01}, the matrix elements in (42) that involve Ψ_{0b},Ψ_{0c}, or a ϕ_i that contains a large component of χ_0, or any other χ_j that is almost orthogonal to χ_{01}, will be very small if the associated δ-function leptonic wave function does not vary with R.

The third term on the right-hand side of (32) does not involve $\Psi_{\mathrm{lep},0}\chi_{01}$ and is thus not influenced by the resonant condition. We can interpret its contribution to $Z_{\mathrm{eff}}(k)$ as being from nonresonant scattering.

V. COMPARISON WITH ANOTHER TREATMENT

It is of interest to compare my treatment with that of Gribakin and Lee [2,3]. Their treatment can be applied to any molecule. If the treatment in [2] is applied to positron scattering by H_2, the scattering wave function is made up of a wave function that describes the scattering of a positron by H_2 in its ground state and a second wave function that describes positron capture into quasibound positron-molecule states. See Eq. (5) in his article. This wave function can be used to derive an expression for $Z_{\mathrm{eff}}(k)$ which is in some ways similar in form to the expression (32) that I obtained earlier. See Eq. (8) in this article.

Gribakin's treatment differs from mine in that he places all of the quasibound states on the same footing, whereas I consider the case when the resonant condition (28) is met for the lowest quasibound state. Thus, in my treatment, the remaining quasibound states are included in the part of the scattering wave function that describes nonresonant scattering. It would be straightforward to extend my treatment to calculate similar expressions to that obtained for d_1 for d_i $(i \neq 1)$, though account would have to be taken, where necessary, of open channels involving excited vibrational states of the target H_2.

Thus, the appropriate comparison with the first term in (32), which is the resonant contribution to $Z_{\mathrm{eff}}(k)$ in my treatment, is with the diagonal element corresponding to the lowest quasibound state with zero total angular momentum in the last term in Eq. (8) in [2]. In keeping with my notation, I take this state to have $\nu = 1$.

The resonant contribution to $Z_{\mathrm{eff}}(k)$, as expressed in terms of this diagonal element, is similar to that obtained by Gribakin and Lee [3] by a direct application of the Breit-Wigner formula. In view of this, I think that it is sufficient to compare my results with those in [3].

The resonant contribution is approximately equal to

$$\frac{\frac{\pi}{k}\rho_{ep}g_1\Gamma_1^e}{(\varepsilon - E_1 - \varepsilon_0)^2 + \frac{\Gamma_1^2}{4}},$$

where ρ_{ep} is the average electron density at the positron in the resonant quasibound state, ε is the incident positron energy, E_1 is the vibrational excitation energy, ε_0 is the positron bound-state energy < 0, and g_1 is the degeneracy of the resonant state, which equals 1 in this case. Γ_1 is the sum of the annihilation width (Γ_1^a) and the capture or elastic width (Γ_1^e).

$\Gamma_1^e = |G|^2\langle\Phi_1|V_p|\Phi_{\mathbf{k}}^{(0)}\rangle|^2$, where G is a constant, Φ_1 is the wave function of the resonant quasibound state, and $\Phi_{\mathbf{k}}^{(0)}$ is the nonresonant scattering wave function in the Born approximation.

In my treatment, the resonant contribution is given approximately by

$$|B|^2\left[\frac{\mu_M(\langle\Psi_{nr} + \Psi_{\mathrm{lep},0}\chi_{01}|V_p|\Psi_{0a}\rangle)}{\langle\Psi_{nr}|\zeta_1+\omega_1\rangle + \mu_M\left(E_{01} - E + \frac{1}{\mu_M}\langle\Psi_{\mathrm{lep},0}\chi_{01}|\omega_1\rangle\right)}\right]^2 \times \langle\Psi_{\mathrm{lep},0}\chi_{01}|\sum_{i=2}^{3}\delta(\mathbf{r}_1-\mathbf{r}_i)|\Psi_{\mathrm{lep},0}\chi_{01}\rangle.$$

$\Psi_{\mathrm{lep},0}\chi_{01}$ corresponds to Φ_1. Using (34), Ψ_{0a} can be taken to be the s-wave component of $\Phi_{\mathbf{k}}^{(0)}$, normalized with respect to the spherical polar angles.

If we compare the two preceding expressions for the resonant contribution to $Z_{\mathrm{eff}}(k)$, we can see that the denominator in the Gribakin and Lee expression is always positive, whereas in my expression it may be zero. Thus, an important difference between the two treatments is that the resonant contribution may be very large in the Gribakin and Lee treatment but it can never be infinite, whereas in my treatment it may be infinite. A further difference between the denominators is that Gribakin and Lee include the annihilation width, Γ_1^a in Γ_1, in addition to the capture width, Γ_1^e. In my treatment, $Z_{\mathrm{eff}}(k)$, which corresponds physically to the normalized probability per unit volume that the positron is located at a target electron, is calculated without inclusion of the annihilation channel in the Kohn calculation. I comment further on this in the Conclusion.

In other respects, however, there are similarities between the two treatments. The factor ρ_{ep} in the numerator of the resonant contribution in the Gribakin and Lee treatment is the average electron density at the positron in the resonant quasibound state. This is closely related to the δ-function matrix element in my expression and in [2] that has the physical interpretation described previously with the system in the resonant quasibound state.

In addition, the capture width, Γ_1^e, which occurs in this numerator, is similar to the matrix element squared

$$[\langle\Psi_{nr} + \Psi_{\mathrm{lep},0}\chi_{01}|V_p|\Psi_{0a}\rangle]^2$$

in the numerator of the resonant contribution in my treatment. In this case, the capture is into a resonant state that contains not only the quasibound, resonant state, $\Psi_{\text{lep},0}\chi_{01}$ but also Ψ_{nr}. The stationary condition this resonant state satisfies will make it nearly an eigenfunction of $\hat{H}_{\text{c.m.}}$ as we are assuming that the basis set used in the Kohn calculation is very flexible. As pointed out earlier, when the energy E is close to the resonant value, Ψ_{nr} will be small as $\Psi_{\text{lep},0}\chi_{01}$ itself will be almost an eigenfunction.

If we use (34) for Ψ_{0a}, and the fact that

$$\chi_{01}(R) \approx \chi_1(R), \tag{45}$$

where $\chi_1(R)$ is the first excited vibrational-state wave function for H_2 and then, for the s wave in the vicinity of the resonance the matrix element $\langle \Psi_{nr} + \Psi_{\text{lep},0}\chi_{01}|V_p|\Psi_{0a}\rangle$ in the numerator of my expression for the resonant contribution to $Z_{\text{eff}}(k)$ will be approximately proportional to $\langle \Phi_1|V_p|\Phi_{\mathbf{k}}^{(0)}\rangle$ in [3]. Thus, except very close to the E value, E_{res}, that makes the resonant contribution to $Z_{\text{eff}}(k)$ infinite in my treatment, the two resonant contributions should show similar behavior with varying E.

Approximations based on the assumption that the weakly bound quasibound states are very diffuse constitute a key feature of the Gribakin and Lee treatment. Using this assumption, they expand V_p in a multipole expansion about the origin. We can do this in the matrix element $\langle \Psi_{\text{lep},0}\chi_{01}|V_p|\Psi_{0a}\rangle$ For the methyl halide target molecules considered in [3], the leading term in the contribution to $\langle \Phi_1|V_p|\Phi_{\mathbf{k}}^{(0)}\rangle$ is the dipole moment term. In the case of H_2, the leading term is the quadrupole moment term as H_2 does not have a permanent dipole moment.

However, if the charges on the nuclei A and B were changed to $1+\Delta Z$ and $1-\Delta Z$, respectively, where $0<\Delta Z<0.3$ (say), the resulting molecule would have a permanent dipole moment and the leading term in the multipole expansion would be the dipole moment term. Alternatively, my treatment could be applied to positron scattering by a heteronuclear diatomic molecule such as CO that has a permanent dipole moment. Retaining only the dipole moment term would now give essentially the same result for the s wave as in Eq. (6) in [3].

Changing the charges on the nuclei in this way would make the vibrational states of the molecule infrared active. See, for example, Atkins and Friedman [13]. This establishes a link with the Gribakin and Lee treatment of the large $Z_{\text{eff}}(k)$ values observed in positron scattering by the methyl halides, CH_3F, CH_3Cl, and CH_3Br, in which the positron capture width plays a key role. Large $Z_{\text{eff}}(k)$ values are associated with capture into quasibound states that are very weakly bound and correspond to infrared-active vibrational levels.

A further difference between the two treatments is that the results in [2] and [3] are obtained without explicitly mentioning corrections to the BO approximation, whereas they are fully taken into account in my treatment. However, the derivation of the approximate expression for d_1 in (40) from the result in (25) obtained from the Kohn equations links V_p with the corrections to the BO approximation, showing that they are implicitly taken into account in [2] and [3].

These BO corrections feature explicitly in the first matrix element in the denominator of my expression for the resonant contribution to $Z_{\text{eff}}(k)$ in my treatment. The BO correction terms and V_p are approximately equivalent in this matrix element if the potential effectively only contributes at long range so that the dominant interaction is with Ψ_{0b} and Ψ_{0c} in Ψ_{nr} which have asymptotic forms as in (14) and (15).

Finally, the treatments in [2] and [3] make clever use of approximate methods for evaluating the resonant contribution to $Z_{\text{eff}}(k)$, whereas very accurate results can be obtained using the Kohn method by using a basis set that can fit the exact scattering wave function very accurately, as is assumed to be the case in my treatment.

VI. CONCLUSION

I have applied the Kohn method to the calculation of $Z_{\text{eff}}(k)$ for positron hydrogen molecule scattering. Particular attention is paid to the contribution from resonant scattering. The mass of the positron is increased so that it forms a weakly bound state with H_2 with its nuclei fixed for all R values for which the associated vibrational wave functions in the BO approximation differ appreciably from zero.

The state associated with the ground vibrational wave function is a bound state in the BO approximation and is assumed to remain bound when corrections to this approximation are taken into account. There exist other states that are bound states in the continuum in the BO approximation. When corrections to the BO approximation are taken into account, these states couple with each other and the continuum. As shown earlier, the coupling between the bound states can be taken into account directly, if desired, by diagonalizing the matrix representation of $\hat{H}_{\text{c.m.}}$ with respect to these states. The coupling to the continuum causes the states to become quasibound. They give rise to vibrational Feshbach resonances [3] at energies just below excited vibrational states of H_2.

The BO approximation is a very good approximation. That is why it is so widely used in theoretical treatments of systems involving molecules. It is because it is such a good approximation that the quasibound states are nearly eigenfunctions of $\hat{H}_{\text{c.m.}}$. In a time-dependent treatment, they would be very long-lived states.

However, at a more fundamental level it is important to bear in mind that the system being considered is five particles interacting through Coulomb forces. As we are working at very low energies, we can apply nonrelativistic quantum mechanics. To carry out a full treatment, we need to know what new terms have to be taken into consideration if no approximations are made in treating the system. This brings in the corrections to the BO approximation. They are clearly important as they bring about the coupling of the quasibound states to the continuum. For this reason, I have taken a full account of these corrections in my treatment.

I consider the simplest case of scattering involving states of zero angular momentum with resonant behavior due to interaction with the lowest quasibound state. In a manner similar to Feshbach [10], I divide the Kohn basis functions into two disjoint subspaces, Γ and $\Gamma^{\perp}$, where Γ has as basis the quasibound states and $\Gamma^{\perp}$ contains all the other functions in the Kohn trial function. I then apply Cramer's rule to the resulting Kohn equations to obtain the coefficient, d_1, of the resonant quasibound state in the scattering wave function.

A further application of Cramer's rule makes it possible to show that the wave function Ψ_{nr}, that features in the expression (25) for d_1, is such that

$$\langle \Psi_{nr} + \Psi_{\text{lep},0}\chi_{01} | \hat{H}_{\text{c.m.}} - E | \Psi_{nr} + \Psi_{\text{lep},0}\chi_{01} \rangle$$

is stationary with respect to variations of the parameters $\{g_i\}_{i=1}^{p-1}$ in Ψ_{nr}. As pointed out earlier, this gives a physical meaning to the wave function $\Psi_{nr} + \Psi_{\text{lep},0}\chi_{01}$.

The expression (25) for d_1 is exact for the Kohn basis set used in the calculation. The basis functions can be chosen to represent the exact wave function very accurately and thus d_1 can be made very accurate. This makes possible the *ab initio* derivation of a very accurate expression for the contribution to $Z_{\text{eff}}(k)$ from a resonant quasibound state.

Ψ_{0a} has the asymptotic form given in relation (13). This form is an eigenfunction of $\hat{H}_{\text{c.m.}} - V_p$, where V_p is given in (36) and is the potential between the target and the positron. It corresponds to a free s-wave positron and the target H_2 molecule. Ψ_{0a} will differ from this asymptotic form as it is contained in $\Gamma^{\perp}$ and is thus orthogonal to all the quasibound states. However, the accuracy of the BO approximation and the fact that the positron is weakly bound mean that, to a good approximation, Ψ_{0a} can be taken to be equal to this asymptotic form. This gives the approximate relation for d_1 in (40).

This relation results from the fact that in the particular case of coupling of a free-particle positron plus target state to a quasibound state, the coupling can, to a good approximation, be regarded as being brought about by V_p. It makes possible a link between my treatment and that of Gribakin and Lee [2,3] as it introduces into the numerator of the approximate form (40) for d_1 the matrix element $\langle \Psi_{\text{lep},0}\chi_{01} | V_p | \Psi_{0a} \rangle$ that is similar to the capture width that is a key feature of their treatment. This shows that they take corrections to the BO approximation into account implicitly, whereas my treatment takes them into account explicitly. The preceding matrix element can be evaluated approximately using the method in [3]. The vibrational mode in the quasibound state can be made infrared-active, as in [3], by changing the charges on the nuclei to $1 + \Delta Z$ and $1 - \Delta Z$, respectively, where $0 < \Delta Z < 0.3$ (say). There is also the alternative option of considering this matrix element in positron scattering by a heteronuclear diatomic molecule such as CO that has a permanent dipole moment and thus has infrared-active vibrational modes. This gives some support to the Gribakin and Lee explanation of the very high $Z_{\text{eff}}(k)$ values that are observed in positron scattering by, for example, methyl halides, as being due to Feshbach resonances involving quasibound states associated with infrared-active vibrational modes.

However, in my treatment V_p couples Ψ_{0a} to the state $\Psi_{nr} + \Psi_{\text{lep},0}\chi_{0N_r}$, though the component Ψ_{nr} is likely to be small in the vicinity of the resonance. This wave function also appears in the first term in the denominator of (40), which represents coupling between it and the resonant quasibound state resulting from corrections to the BO approximation. This term differs from the corresponding term in the Gribakin and Lee treatment, but it may be possible to establish some relationship between them using the approximate methods used in [3].

The most important difference between my treatment and the treatments in [2] and [3] is that in my treatment $Z_{\text{eff}}(k)$ may be infinite, whereas this is not possible in the other treatments. The infinite value results from a rigorous application of the Kohn variational method. However, the calculation of the positron annihilation rate, λ, using $Z_{\text{eff}}(k)$ is carried out using first-order perturbation theory, as it is assumed that the interaction involved is very weak [14]. It may be that this assumption breaks down in the vicinity of a resonance, resulting in the infinite value. If so, it might be necessary to include the annihilation channel explicitly in the trial function and calculate the annihilation cross section, and hence the annihilation rate, directly from the asymptotic form of the wave function. Further investigation is required. However, the infinity in $Z_{\text{eff}}(k)$ would not occur if Ψ_{0b} and Ψ_{0c} were complex functions. The significance of this also needs to be investigated. Note that the associated infinite value of d_1 will give rise to resonant behavior in the phase shift as the expectation value of $\hat{H}_{\text{c.m.}} - E$ over the trial function occurs in the expression for the tangent of the phase shift in the Kohn method. This can most simply be seen if we neglect mixing of partial waves in the molecule-fixed frame [9].

It is possible that difficulties could arise in solving (17) or (A7) due to ill conditioning of the matrix A or $\bar{A}$. These could be taken into account using the generalized Kohn method. A detailed, mathematical treatment of the results obtained using the generalized Kohn method is given in [15].

The same scattering wave function would be obtained if the square-integrable basis functions in the trial function were subjected to any nonsingular, linear transformation. Thus the overall value calculated for $Z_{\text{eff}}(k)$ would remain the same, but it would not, in general, be possible to highlight the resonant contribution from a given quasibound state.

I have assumed in my treatment that the weakly bound state that I introduce by increasing the mass m_p of the positron is bound for all R values for which the associated vibrational wave function differs appreciably from zero. If this is not the case for a subset of these R values, it might be possible to use an eigendifferential with a narrow energy span above the continuum threshold to represent the leptonic wave function at these R values (see, for example, Messiah [16]).

My treatment could be straightforwardly applied to the scattering of higher partial waves and also to resonances involving higher-energy quasibound states. Treatment of such resonances would require inclusion of open channels involving excited vibrational states of H_2 that are lower in energy than the quasibound state responsible for the resonance under consideration. My treatment could also be applied to resonances due to quasibound states that do not owe their existence to the accuracy of the BO approximation.

Finally, I have considered scattering of a positron by H_2 as this is the simplest molecular target. The mass of the positron is increased so that it forms a weakly bound state with H_2. The simplicity of the target makes it easier to identify the various corrections to the BO approximation and apply the Kohn variational method to calculate the resonant contribution to $Z_{\text{eff}}(k)$ from a given quasibound state. There is no reason, in principle, why my treatment cannot be extended to target molecules such as methyl halides whose very high $Z_{\text{eff}}(k)$ values can be explained if these molecules can form weakly bound states with a positron [3]. However, such calculations would necessarily be considerably more complicated.

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APPENDIX

A_{ij} denotes the element in the ith row and jth column of the matrix A. The cofactor A'_{ip} in (24) is given by

$$A'_{ip} = (-1)^{i+p} \begin{vmatrix} A_{11} & A_{12} & \cdots & \cdots & A_{1p-1} \\ A_{21} & A_{22} & \cdots & \cdots & A_{2p-1} \\ \vdots & \vdots & & & \vdots \\ A_{i-11} & A_{i-12} & \cdots & \cdots & A_{i-1p-1} \\ A_{i+11} & A_{i+12} & \cdots & \cdots & A_{i+1p-1} \\ \vdots & \vdots & & & \vdots \\ A_{p-11} & A_{p-12} & \cdots & \cdots & A_{p-1p-1} \\ A_{p1} & A_{p2} & \cdots & \cdots & A_{p\,p-1} \end{vmatrix} (i < p = N + N_r + 2) \tag{A1}$$

$$= (-1)^{i+p+p-1-i} \begin{vmatrix} A_{11} & A_{12} & \cdots\cdots & A_{1p-1} \\ A_{21} & A_{22} & \cdots\cdots & A_{2p-1} \\ \vdots & \vdots & & \vdots \\ A_{i-11} & A_{i-12} & \cdots\cdots & A_{i+1p-1} \\ A_{p1} & A_{p2} & \cdots\cdots & A_{p\,p-1} \\ A_{i+11} & A_{i+12} & \cdots\cdots & A_{i+1p-1} \\ \vdots & \vdots & & \vdots \\ A_{p-11} & A_{p-12} & \cdots\cdots & A_{p-1,p-1} \end{vmatrix} (i < p). \tag{A2}$$

Using the fact that the determinant of a matrix equals the determinant of its transpose and A is a real, symmetric matrix, A'_{ip} can be expressed in the form

$$A'_{ip} = - \begin{vmatrix} A_{11} & A_{12} & \cdots & A_{1i-1} & A_{1p} & A_{1i+1} & \cdots & A_{1p-1} \\ A_{21} & A_{22} & \cdots & A_{2i-1} & A_{2p} & A_{2i+1} & \cdots & A_{2p-1} \\ \vdots & \vdots & & \vdots & \vdots & \vdots & & \vdots \\ A_{p-11} & A_{p-12} & \cdots & A_{p-1i-1} & A_{p-1p} & A_{p-1i+1} & \cdots & A_{p-1p-1} \end{vmatrix} (i < p). \tag{A3}$$

Also, if $i = p$

$$A'_{pp} = \begin{vmatrix} A_{11} & A_{12} & \cdots & A_{1p-1} \\ A_{21} & A_{22} & \cdots & A_{2p-1} \\ \vdots & \vdots & & \vdots \\ A_{p-11} & A_{p-12} & \cdots & A_{p-1p-1} \end{vmatrix}. \tag{A4}$$

The wave function Ψ_{nr} is of the form

$$\Psi_{nr} = g_1\Psi_{0b} + g_2\Psi_{0c} + g_3\phi_1 + \cdots + g_{N+2}\phi_N + \sum_{i=N+3}^{p-1} g_i \Psi_{\text{lep},0}\chi_{0j} \quad (j = i - N - 1), \tag{A5}$$

where

$$g_i = \frac{A'_{ip}}{A'_{pp}} \qquad (i < p). \tag{A6}$$

We can see from (A3), (A4), and (A6) that it follows from Cramer's rule that the coefficients $\{g_i\}_{i=1}^{p-1}$ satisfy the linear, inhomogeneous equations

$$\bar{A}g = -h, \tag{A7}$$

where $\bar{A}$ is the matrix with elements $A_{ij}(i,j < p)$ and

$$\begin{aligned} h &= [A_{1p}A_{2p}\cdots A_{p-1p}]^\top \\ &= \frac{1}{\mu_M}\big[\langle\Psi_{0b}|\zeta_1\rangle\langle\Psi_{0c}|\zeta_1\rangle\langle\phi_1|\zeta_1\rangle\cdots\langle\phi_N|\zeta_1\rangle \\ &\qquad \langle\omega_{N_r}|\Psi_{\text{lep},0}\chi_{01}\rangle\cdots\langle\omega_2|\Psi_{\text{lep},0}\chi_{01}\rangle\big]^\top. \end{aligned} \tag{A8}$$

These are the equations that determine the coefficients $\{g_i\}_{i=1}^{p-1}$ such that

$$\langle\Psi_{nr} + \Psi_{\text{lep},0}\chi_{01}|\hat{H}_{\text{c.m.}} - E|\Psi_{nr} + \Psi_{\text{lep},0}\chi_{01}\rangle$$

is stationary with respect to variations of these coefficients.

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