Stochastic variational calculation of zero-energy positron scattering from H, He, and H₂

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The confined variational method is used to generate a set of energy-optimized explicitly correlated Gaussians to describe positrons interacting with H, He and the H₂ molecule. These basis functions are then used in a Kohn variational calculation of the scattering lengths and zero-energy annihilation parameters, Z_{eff}. The results for the H and He atoms are consistent with previous high-quality variational calculations while the annihilation parameter for H₂ is consistent with experiment. An extensive tabulation of the H₂ scattering parameters as a function of internuclear distance confirm the existence of a virtual state at $R \approx 3.4a_0$. The scattering length was $-2.71a_0$ and Z_{eff} was 15.7 at the mean H₂ internuclear distance of $1.45a_0$.

I. INTRODUCTION

One of the most important developments in few-body physics in the last decade has been the increasing use of variational methods using explicitly correlated Gaussians (ECGs) as basis functions [1–3]. Calculations have been carried out in the area of subnuclear physics [4], nuclear physics [5,6], atomic physics [7], condensed-matter physics [8], and quantum chemistry [9,10]. Two of the more startling results were the discovery that many neutral atoms could form electronic stable states with a positron [11,12] and the recent calculations on small molecules going beyond the Born-Oppenheimer approximation [10].

The reason for the explosion of calculations using ECG basis sets comes from their algebraic properties. Quite simply, the matrix elements of the Hamiltonian between two different ECG basis functions are algebraically compact and straightforward to compute. Coupled with the fact that the memory requirements of a typical calculation are relatively modest, this means that close to exact calculations for many-body systems containing 4–5 particles are feasible with modest computational resources.

In this paper, we apply ECG basis sets to the scattering of positrons from small atoms and molecules within the framework of the Kohn variational method. This represents a natural evolution in technique from earlier scattering work using ECG basis functions. An early application used stabilization ideas to get low-energy phase shifts for positronium-atom scattering [13]. Since that time, confining potentials have been added to the scattering Hamiltonian to generate ECG basis sets optimized to give a good description in the interaction region [14–16]. In addition, alternatives to the stabilization approach have been developed to extract the phase shift [16]. Most recently, a confining potential plus stabilization method was used to compute the scattering length for e^+-H₂ scattering [17]. A common feature of all these methods is that they generate phase shifts at low but finite energies (although effective range theory can be used to estimate zero-energy scattering parameters).

The present paper is specialized to zero-energy scattering and is restricted to the computation of the scattering length

and the zero-energy positron annihilation parameter Z_{eff}. The confined variational method (CVM) [15,16] was initially used to generate an energy-optimized ECG basis in the interaction region. These basis functions were then used in zero-energy Kohn variational calculations of positron scattering from H, He, and H₂. Scattering lengths accurate to a couple of percent were obtained for all systems. The calculations for H₂ were undertaken in the fixed nuclei approximation.

II. DETAILS OF THE METHOD

A. The scattering Hamiltonian

In this paper the analysis is confined to a positron colliding with a neutral atom or molecule with infinitely heavy nuclei. Significant computational simplifications occur when the scattering particle is a positron since the exchange interaction between projectile and target is absent.

1. The hydrogen and helium atoms

The Hamiltonian for a positron colliding with a helium atom with nuclear charge $Z = 2$ and with $N = Z = 2$ target electrons is

$$H = -\sum_{i=1}^{N} \frac{1}{2} \nabla_i^2 - \frac{1}{2} \nabla_{N+1}^2 - \sum_{i=1}^{N} \frac{Z}{r_i} + \frac{Z}{r_{N+1}}$$
$$+ \sum_{i<j}^{N} \frac{1}{r_{ij}} - \sum_{i=1}^{N} \frac{1}{r_{N+1,i}}. \tag{1}$$

In this expression, particle $(N + 1)$ is identified as the scattering particle and is a positron. All the other particles are electrons. It is convenient to partition the Hamiltonian as

$$H = H_{N+1} + H_{\text{atom}}, \tag{2}$$

where

$$H_{N+1} = -\frac{1}{2} \nabla_{N+1}^2 + \frac{Z}{r_{N+1}} - \sum_{i=1}^{N} \frac{1}{r_{N+1,i}} \tag{3}$$

is the Hamiltonian for the scattering particle and

$$H_{\text{atom}} = -\sum_{i=1}^{N} \frac{1}{2} \nabla_i^2 - \sum_{i=1}^{N} \frac{Z}{r_i} + \sum_{i<j}^{N} \frac{1}{r_{ij}} \tag{4}$$

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is the Hamiltonian for the atomic target. The function $|\Phi_0\rangle$ is the wave function for the target ground state and is expanded as a linear combination of N_0 ECGs, viz.

$$|\Phi_0\rangle = \sum_{k=1}^{N_0} b_k \exp\left(-\frac{1}{2}\sum_{i=1,j=1}^{N} B_{ij}^k \, \mathbf{r}_i \cdot \mathbf{r}_j\right). \qquad (5)$$

This wave function represents a stationary state satisfying

$$\langle\Phi_0|H_{\mathrm{atom}}|\Phi_0\rangle = \epsilon_0. \qquad (6)$$

The ground-state wave function is generated using the stochastic variational method (SVM) [6,12,18]. This wave function is *not* an exact eigenstate, but for all practical purposes can be regarded as an eigenstate so the relation,

$$H_{\mathrm{atom}}|\Phi_0\rangle = \epsilon_0|\Phi_0\rangle, \qquad (7)$$

can be assumed without risk of any significant error.

2. The hydrogen molecule

The Hamiltonian for $e^+\mathrm{H}_2$ scattering with $N = 2$ electrons and one positron can be written

$$H = -\sum_{i=1}^{N+1}\frac{\nabla_i^2}{2} - \sum_{i=1}^{N}\frac{1}{|\mathbf{r}_{N+1}-\mathbf{r}_i|}$$
$$+ \frac{1}{|\mathbf{r}_1-\mathbf{r}_2|} + \frac{1}{|\mathbf{r}_{N+1}-\mathbf{R}/2|} + \frac{1}{|\mathbf{r}_{N+1}+\mathbf{R}/2|}$$
$$- \sum_{i=1}^{N}\left(\frac{1}{|\mathbf{r}_i+\mathbf{R}/2|} + \frac{1}{|\mathbf{r}_i-\mathbf{R}/2|}\right) + \frac{1}{R}. \qquad (8)$$

The vector $\mathbf{R}/2$ is the displacement of the two protons from the midpoint of the molecular axis. This Hamiltonian can likewise be partitioned into a molecular Hamiltonian just involving the electrons and the positron Hamiltonian, for example,

$$H = H_{N+1} + H_{\mathrm{molec}}, \qquad (9)$$

where the positron-molecule Hamiltonian H_{N+1} is

$$H_{N+1} = -\frac{1}{2}\nabla_{N+1}^2 - \sum_{i=1}^{N}\frac{1}{|\mathbf{r}_{N+1}-\mathbf{r}_i|}$$
$$+ \frac{1}{|\mathbf{r}_{N+1}-\mathbf{R}/2|} + \frac{1}{|\mathbf{r}_{N+1}+\mathbf{R}/2|}, \qquad (10)$$

and the target Hamiltonian is

$$H_{\mathrm{molec}} = -\sum_{i=1}^{N}\frac{\nabla_i^2}{2} + \frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}$$
$$- \sum_{i=1}^{N}\left(\frac{1}{|\mathbf{r}_i+\mathbf{R}/2|} + \frac{1}{|\mathbf{r}_i-\mathbf{R}/2|}\right) + \frac{1}{R}. \qquad (11)$$

The wave function, $|\Phi_0\rangle$, of the H_2 ground state is written as a linear combination of ECGs with shifts, for example,

$$\Phi_k = \hat{P}\,\exp\left(-\frac{1}{2}\sum_{i=1}^{2} B_{k,i}|\mathbf{r}_i-\mathbf{s}_{k,i}|^2\right)$$
$$\times \exp\left(-\frac{1}{2}A_k|\mathbf{r}_1-\mathbf{r}_2|^2\right). \qquad (12)$$

The vector $\mathbf{s}_{k,i}$ displaces the center of the ECG for the ith particle to a point on the internuclear axis. This ensures the three-particle wave function is of Σ symmetry. The values of a_k, $b_{k,i}$, and $\mathbf{s}_{k,i}$ are adjusted during the optimization process. The operator $\hat{P}$ is used to enforce Σ_g symmetry. This is done by generating each basis function as a combination of two ECGs. Once $\mathbf{s}_{k,i}$ is set, another ECG with $\mathbf{s}_{k,i} \to -\mathbf{s}_{k,i}$ is added. The pair of basis functions have the same linear coefficient for a state of Σ_g symmetry (the coefficients would have opposite signs in the case of Σ_u symmetry). Each ECG has a total of five stochastically adjustable parameters. This wave function is a stationary state satisfying

$$\langle\Phi_0|H_{\mathrm{molec}}|\Phi_0\rangle = \epsilon_0. \qquad (13)$$

The ground-state wave function is *not* an exact eigenstate, but for all practical purposes can be regarded as an eigenstate.

B. The confining potential

The first stage of the scattering calculations use the confined variational method (CVM) [15,16]. A single-body confining operator V_{CP} is added to the system Hamiltonian. The potential is written

$$V_{\mathrm{CP}} = \sum_{i=1}^{N+1} \lambda(r_i - R_0)^2 \Theta(r_i - R_0), \qquad (14)$$

where $\Theta(r - R_0)$ is a Heaviside function and λ is a small positive number.

The operator as implemented acts on all particles. Since the projectile is a positron, it would be possible to have V_{CP} only acting on the positron. The values chosen for the confining radius R_0 are sufficiently large for the impact of V_{CP} on the target electron wave functions to be minute.

Calculations with the CVM are used to generate a basis of ECGs that gives a good description of the target + projectile wave function when the projectile is close to the target. The basis is optimized by minimizing the energies of the lowest few states.

C. The Kohn variational method

The scattering length will be determined with the Kohn variational method [19–21] with ECGs as trial functions. The formalism presented here closely follows that outlined in the monograph of Burke and Joachain [22].

Ignoring symmetry considerations for the moment, the trial wave function adopted for the present Kohn variational calculations have the form,

$$|\Psi_t\rangle = |\Psi_0\rangle + A_t|\Psi_1\rangle + \sum_{i=2}^{n} c_i|\Psi_i\rangle, \qquad (15)$$

where there are two types of $(N + 1)$-particle short-range basis functions. The first type consists of a set of simple ECGs,

$$|\Psi_m^{\mathrm{I}}\rangle = \exp\left(-\frac{1}{2}\sum_{i=1,j=1}^{N+1} \mathbf{r}_i \cdot \mathbf{r}_j P_{ij}^m\right). \qquad (16)$$

For the H_2 molecular target, these basis functions are similar to the Φ_k of Eq. (12) and are written

$$\left|\Psi_m^{\mathrm{I}}\right\rangle = \exp\left(-\frac{1}{2}\sum_{i=1,j=1}^{N+1}(\mathbf{r}_i - \mathbf{s}_i)\cdot(\mathbf{r}_j - \mathbf{s}_j)P_{ij}^m\right). \quad (17)$$

Type I basis functions are generated during the stochastic optimization of the confined system. The second type consists of a composite functions with

$$\left|\Psi_m^{\mathrm{II}}\right\rangle = \exp\left(-\tfrac{1}{2}\alpha r_{N+1}^2\right)|\Phi_0\rangle. \quad (18)$$

Type II basis functions were found to greatly improve the precision of phase shifts computed using the CVM [15,16] since they help embed a close to exact description of the target into the trial wave function. In the case of a molecular target, some additional molecular-type positron orbitals were also included in the type II basis. These positron orbitals are constructed to have Σ_g symmetry and had the form,

$$\begin{aligned}\left|\Psi_m^{\mathrm{II}}\right\rangle &= \big[\exp\left(-\tfrac{1}{2}\alpha\left(\mathbf{r}_{N+1}-\mathbf{s}\right)^2\right)\\&\quad+\exp\left(-\tfrac{1}{2}\alpha\left(\mathbf{r}_{N+1}+\mathbf{s}\right)^2\right)\big]|\Phi_0\rangle. \end{aligned} \quad (19)$$

The two functions with continuum boundary conditions for the positron are

$$|\Psi_0\rangle = |\Phi_0\rangle, \quad (20)$$

$$|\Psi_1\rangle = \frac{\left[1-\exp\left(-\beta r_{N+1}^2\right)\right]}{r_{N+1}}|\Phi_0\rangle, \quad (21)$$

where the $|\Phi_0\rangle$ are written as linear combinations of ECGs. The constant A_t in Eq. (15) is the first-order value of the scattering length while the $[1-\exp(-\beta r_{N+1}^2)]$ prefactor ensures that the scattering wave function is regular at the origin. The scattering length will be relatively insensitive to the values of β provided the basis of short-range functions is of sufficient quality.

The scattering wave function is given by the condition that the Kohn functional A defined by

$$\begin{aligned}A &= A_t - 2\langle\Psi_t|H-\epsilon_0|\Psi_t\rangle\\&= A_t - 2I_{tt}\end{aligned} \quad (22)$$

is stationary. The right-hand side of the Kohn functional, contains $(H-\epsilon_0)$ rather than $(H-E)$ since we are concerned with scattering at zero energy. Making the Kohn functional stationary with respect to the linear variational parameters in the trial wave function leads to the linear equations:

$$\frac{\partial A}{\partial A_t} = 1 - 2\frac{\partial I_{tt}}{\partial A_t}, \quad (23)$$

$$\frac{\partial A}{\partial c_i} = 0 = -2\frac{\partial I_{tt}}{\partial c_i}. \quad (24)$$

These equations are solved to determine A_t and c_i. The error in A_t upon solving the set of n linear equations is of first order with respect to variations in the trial wave function. The notation $I_{ij} = \langle\Psi_i|H-\epsilon_0|\Psi_j\rangle$ is adopted. If either of the subscripts is 1 or 0 then the matrix elements involve at least one long-range basis function. Using the variational conditions, Eq. (24), leads to a set of n simultaneous linear equations:

$$\begin{array}{l}\frac{\partial I_{tt}}{\partial A_t}\rightarrow\\\frac{\partial I_{tt}}{\partial c_2}\rightarrow\\\vdots\\\frac{\partial I_{tt}}{\partial c_n}\rightarrow\end{array}\begin{bmatrix}2I_{11} & \cdots & I_{1n}+I_{n1}\\I_{21}+I_{12} & \cdots & I_{2n}+I_{n2}\\\vdots & \cdots & \vdots\\I_{n1}+I_{1n} & \cdots & 2I_{nn}\end{bmatrix}\begin{bmatrix}A_t\\c_2\\\vdots\\c_n\end{bmatrix}=\begin{bmatrix}\frac{1}{2}-(I_{10}+I_{01})\\-(I_{20}+I_{02})\\-(I_{30}+I_{03})\\\vdots\\-(I_{n0}+I_{0n})\end{bmatrix}. \quad (25)$$

All the scattering lengths A reported in this paper are computed with Eq. (22) since the the error in A is of second order with respect to variations in the trial wave function.

D. General expressions for ECG matrix elements

The matrix element evaluations require a detailed knowledge of the structure of the different classes of basis functions. The present calculations are performed under the condition that the nucleus is infinitely heavy.

The properties of a general ECG are now introduced to be used later. The following identities are taken from the literature [3] without derivation. The function G is defined as

$$G(P,N+1,\mathbf{s}) = \exp\left(-\tfrac{1}{2}\mathbf{r}^T P\mathbf{r}+\mathbf{s}^T\cdot\mathbf{r}\right), \quad (26)$$

where

$$\mathbf{r}^T P\mathbf{r} = \sum_{i=1,j=1}^{N+1}\mathbf{r}_i\cdot\mathbf{r}_j P_{ij}, \quad (27)$$

and $\mathbf{s}$ is a set of translation vectors,

$$\mathbf{s}^T\cdot\mathbf{r} = \sum_{i=1}^{N+1}\mathbf{s}_i\cdot\mathbf{r}_i = \sum_{i=1}^{N+1}\mathbf{r}_i\cdot\mathbf{s}_i. \quad (28)$$

The dimensionality of the P matrix is larger by one than the dimensionality of the B matrices in Eqs. (5) and (12). The ECGs for atomic systems do not involve the use of translation vectors. For notational reasons, the argument of $(N+1)$ will be omitted and the omission of $\mathbf{s}$ from the argument list means $\mathbf{s} = 0$.

The overlap between two ECGs is

$$O(P',\mathbf{s}',P,\mathbf{s}) = \langle G(P',\mathbf{s}')|G(P,\mathbf{s})\rangle = \left(\frac{(2\pi)^{N+1}}{\det(P+P')}\right)^{\frac{3}{2}}$$

$$\times \exp\left[\frac{1}{2}(\mathbf{s}+\mathbf{s}')^T(P+P')^{-1}(\mathbf{s}+\mathbf{s}')\right]. \tag{29}$$

The matrix element of the kinetic energy is

$$\langle G(P',\mathbf{s}')| \sum_{i=1}^{N+1} \frac{\nabla_i^2}{2} |G(P,\mathbf{s})\rangle$$

$$= O(P',\mathbf{s}',P,\mathbf{s})\left[\frac{3}{2}\text{Tr}(P(P+P')^{-1}P')\right.$$

$$- [P'(P'+P)^{-1}\mathbf{s} - P(P'+P)^{-1}\mathbf{s}']^T$$

$$\times \left. [P'(P'+P)^{-1}\mathbf{s} - P(P'+P)^{-1}\mathbf{s}']\right]. \tag{30}$$

The kinetic energy of the scattering particle is

$$\langle G(P',\mathbf{s}')| \frac{\nabla_{N+1}^2}{2} |G(P,\mathbf{s})\rangle$$

$$= O(P',\mathbf{s}',P,\mathbf{s})\frac{3}{2}\text{Tr}[P(P+P')^{-1}P'\Lambda_{N+1}], \tag{31}$$

where Λ_{N+1} is a matrix with all elements set to zero except the $(N+1),(N+1)$ element which is set to 1.

The matrix elements of a one-body operator are derived using the identities,

$$V(\mathbf{r}_i) = \int d^3u \, V(\mathbf{u})\delta(\mathbf{r}_i - \mathbf{u}), \tag{32}$$

and

$$\langle G(P')|\delta(\mathbf{r}_i - \mathbf{u})|G(P)\rangle = O(P',P)\left(\frac{c_i}{2\pi}\right)^{\frac{3}{2}}\exp\left(-\frac{1}{2}c_i u^2\right), \tag{33}$$

to give

$$\langle G(P')|V(r_i)|G(P)\rangle$$

$$= O(P',P)\left(\frac{c_i}{2\pi}\right)^{\frac{3}{2}}\int V(u)\exp\left(-\frac{1}{2}c_i u^2\right)d^3u, \tag{34}$$

with

$$\frac{1}{c_i} = \mathbf{w}^{T,(i)}(P+P')^{-1}\mathbf{w}^{(i)}. \tag{35}$$

The vector $\mathbf{w}^{(i)}$ is defined by $\mathbf{w}_k^{(i)} = \delta_{ik}$ ($k = 1,\ldots,N+1$). If the operator V is a simple power of r, then

$$\langle G(P')|r_i^\alpha|G(P)\rangle = O(P',P)\frac{2}{\sqrt{\pi}}\left(\frac{2}{c_i}\right)^{\frac{\alpha}{2}}\Gamma\left(\frac{\alpha+3}{2}\right), \tag{36}$$

where Γ is the Gamma function.

The matrix element of the two-body potential is given by

$$\langle G(P')|V(\mathbf{r}_i - \mathbf{r}_j)|G(P)\rangle$$

$$= O(P',P)\left(\frac{c_{ij}}{2\pi}\right)^{\frac{3}{2}}\int V(\mathbf{r})\exp\left(-\frac{1}{2}c_{ij}r^2\right)d^3r, \tag{37}$$

where

$$\frac{1}{c_{ij}} = \widetilde{\mathbf{w}^{(ij)}}(P+P')^{-1}\mathbf{w}^{(ij)}. \tag{38}$$

The vector $\mathbf{w}^{(ij)}$ is defined by $\mathbf{w}_k^{(ij)} = \delta_{ik} - \delta_{jk}$ ($k = 1,\ldots,N+1$). The matrix element of the total potential energy is easily obtained by summing Eq. (33) over i, j. As a byproduct of Eq. (33), the matrix element of $|\mathbf{r}_i - \mathbf{r}_j|^\alpha$ is obtained since Eq. (33) can be reduced to

$$\langle G(P')||\mathbf{r}_i - \mathbf{r}_j|^\alpha|G(P)\rangle$$

$$= O(P',P)\frac{2}{\sqrt{\pi}}\left(\frac{2}{c_{ij}}\right)^{\frac{\alpha}{2}}\Gamma\left(\frac{\alpha+3}{2}\right), \tag{39}$$

where c_{ij} is given by Eq. (38).

It is also necessary to evaluate the potential field produced by a spherically symmetric ECG. This is expressed as integrals of the type,

$$\langle G(P')|V(\mathbf{r} - \mathbf{r}_j)|G(P)\rangle$$

$$= O(P',P)\left(\frac{c_j}{2\pi}\right)^{\frac{3}{2}}\int V(|\mathbf{r} + \mathbf{u}|)\exp\left(-\frac{1}{2}c_j r^2\right)d^3u. \tag{40}$$

The methods for evaluating and applying this integral are discussed later.

Potential matrix elements involving shifts are more complicated to evaluate. The fundamental formula is

$$\langle G(P',\mathbf{s}')||\mathbf{r}_i - \mathbf{r}_j|^\alpha|G(P,\mathbf{s})\rangle$$

$$= O(P',\mathbf{s}',P,\mathbf{s})\left(\frac{c_{ij}}{2\pi}\right)^{\frac{1}{2}}\frac{\exp\left(-\frac{1}{2}cs^2\right)}{s}$$

$$\times \int_0^\infty x^{\alpha+1}e^{-\frac{1}{2}cx^2}(e^{csx} - e^{-csx})\,dx, \tag{41}$$

where $s = |\widetilde{\mathbf{w}^{(ij)}}(P+P')^{-1}(\mathbf{s}'+\mathbf{s})|$. This matrix element reduces to the form,

$$\langle G(P',\mathbf{s}')||\mathbf{r}_i - \mathbf{r}_j|^\alpha|G(P,\mathbf{s})\rangle$$

$$= O(P',\mathbf{s}',P,\mathbf{s})\frac{1}{s}\text{erf}\left(\sqrt{\frac{c_{ij}}{2}}s\right), \tag{42}$$

when $\alpha = -1$. When $\sqrt{\frac{c_{ij}}{2}}s$ is very small ($<5 \times 10^{-3}$) a finite number of terms of the power series representation of the error function are used to approximate the numerator of the $\frac{1}{s}\text{erf}(\sqrt{\frac{c_{ij}}{2}}s)$ quotient.

E. Confining potential matrix elements

For atoms, the matrix element of the confining potential between two ECGs is

$$\langle G(P')|V_{CP}(r_i)|G(P)\rangle = \lambda O(P',P)\sqrt{\frac{2}{\pi}}\sum_i c_i^{\frac{3}{2}}$$

$$\times \int_{R_0}^\infty r_i^2(r_i - R_0)^2 \exp\left(-\frac{c_i}{2}r_i^2\right)dr_i, \tag{43}$$

where c_i is given by Eq. (35). The one-dimensional integral on the right-hand side is precomputed for a range of values of the exponent. The basic integral is defined as

$$\text{Int}(a) = (2a)^3 \int_{R_0}^{\infty} r^2 (r - R_0)^2 \exp\left[-a\left(r^2 - R_0^2\right)\right] dr. \quad (44)$$

This integral is done by mapping the $x \in [-1.0, 1.0]$ interval to the $r \in [R_0, \infty)$ interval using the transformation,

$$r = R_0 + \frac{r_a(1 + x)}{1 - x}. \quad (45)$$

The parameter R is chosen to achieve its maximum when the integrand of Eq. (44) achieves its maximum. Gaussian quadratures are then used to integrate x_i over the $[-1.0, 1.0]$ interval.

The integral $\text{Int}(a_i)$ is tabulated with $a_{i+1} = 1.00011 a_i$, with the value of a ranging between 2.0×10^{-4} and 2.0×10^{6}. Values of $\text{Int}(a)$ at arbitrary a are interpolated using Everett's formula for the logarithmically equally spaced values of a. The level of accuracy achieved exceeds the need of the present calculation. This algorithm was designed for the confined variational method which requires very accurate estimates of the total energies of the confined system [14].

For the H_2 molecule, the matrix elements of the confining potential are

$$\langle V_{\text{CP}}(r_i) \rangle = \lambda O(P', \mathbf{s}', P, \mathbf{s}) \sqrt{\frac{c_i}{2\pi}} \sum_i \frac{1}{s_i} \exp\left(-\frac{1}{2} c_i s_i^2\right)$$

$$\times \int_{R_0}^{\infty} r_i (r_i - R_0)^2 \exp\left(-\frac{1}{2} c_i r_i^2\right)$$

$$\times (\exp(c_i s_i r_i) - \exp(-c_i s_i r_i)) \, dr_i, \quad (46)$$

where $s_i = |\widetilde{w^{(i)}}(P + P')^{-1}(\mathbf{s}' + \mathbf{s})|$. The terms in the sum reduce to

$$I_{\text{CP}+} = \frac{1}{s} \exp\left(-\frac{1}{2} c\left(s^2 + R_0^2 + 2sR_0\right)\right) \int_0^{\infty} r^2 (r + R_0)$$

$$\times \exp\left(-\frac{1}{2} cr^2 - cR_0 r + csr\right) dr, \quad (47)$$

and

$$I_{\text{CP}-} = \frac{1}{s} \exp\left(-\frac{1}{2} c\left(s^2 + R_0^2 + 2sR_0\right)\right) \int_0^{\infty} r^2 (r + R_0)$$

$$\times \exp\left(-\frac{1}{2} cr^2 - cR_0 r - csr\right) dr. \quad (48)$$

The basic integral to be done is of the type,

$$\int_0^{\infty} r^n \exp(-ar^2 - br) \, dr$$

$$= a^{-\frac{n+1}{2}} \int_0^{\infty} r^n \exp\left(-r^2 - \frac{b}{\sqrt{a}} r\right) dr. \quad (49)$$

The integral $f(n,a) = \int_0^{\infty} r^n \exp(-r^2 - ar) dr$ can be evaluated analytically [3]. Therefore, we calculate a series of $f(2,a)$ and $f(3,a)$ values while a varies from -30.0 to 4.0×10^3 with the equal interval $h = 5.0 \times 10^{-3}$. Then $f(n,b)$ are interpolated with Everett's formula for $2 \leqslant n \leqslant 3$ and $b \in (-30.0, 4.0 \times 10^3)$.

F. The matrix elements of the Kohn matrix

1. Atomic systems

With these definitions we are in a position to write down explicit expressions for all the matrix elements of the Kohn functional. First it is desirable to introduce the auxiliary function for an electrically neutral atom,

$$V_{N+1}(\mathbf{r}_{N+1}) = \langle \Phi_0| \sum_{i=1}^{N} \left(\frac{1}{r_{N+1}} - \frac{1}{r_{N+1,i}}\right) |\Phi_0\rangle$$

$$= \sum_{i=1}^{N} \sum_{j=1}^{N} b_i b_j \left(\frac{(2\pi)^N}{\det(B^i + B^j)}\right)^{\frac{3}{2}}$$

$$\times \sum_{k=1}^{N} \frac{1}{r_{N+1}} \text{erfc}\left(\sqrt{\frac{c_{ijk}}{2}} r_{N+1}\right), \quad (50)$$

since this is common to a number of the full $(H - \epsilon_0)$ matrix elements. This function has the property that $V_{N+1} \to 0$ as $r_{N+1} \to 0$.

The matrix element $I_{00} = \langle \Psi_0|(H - \epsilon_0)|\Psi_0\rangle$ involving the two continuum functions simplifies because the total energy is zero, giving

$$I_{00} = \int d^3 r_{N+1} \, V_{N+1}(\mathbf{r}_{N+1})$$

$$= \sum_{i=1}^{N} \sum_{j=1}^{N} b_i b_j \left(\frac{(2\pi)^N}{\det(B^i + B^j)}\right)^{\frac{3}{2}}$$

$$\times \sum_{k=1}^{N} \int d^3 r_{N+1} \frac{1}{r_{N+1}} \text{erfc}\left(\sqrt{\frac{c_{ijk}}{2}} r_{N+1}\right)$$

$$= \sum_{i=1}^{N} \sum_{j=1}^{N} b_i b_j \left(\frac{(2\pi)^N}{\det(B^i + B^j)}\right)^{\frac{3}{2}} \sum_{k=1}^{N} \frac{2\pi}{c_{ijk}}, \quad (51)$$

where we have used the fact that the kinetic energy of the scattering particle is zero. The other continuum integral I_{11} is

$$I_{11} = \langle \Psi_1| -\frac{1}{2} \nabla_{N+1}^2 |\Psi_1\rangle + \int d\Omega_{N+1} \int dr_{N+1}$$

$$\times \left[1 - \exp\left(-\beta r_{N+1}^2\right)\right]^2 V_{N+1}(\mathbf{r}_{N+1}). \quad (52)$$

The kinetic energy integral, $T_{11} = \langle \Psi_1| -\frac{\nabla_{N+1}^2}{2} |\Psi_1\rangle$, is

$$T_{11} = 4\pi \langle \Phi_0|\Phi_0\rangle \int d^3 r_{N+1} (2\beta^2 r^2 - \beta)$$

$$\times \left[\exp\left(-\beta r_{N+1}^2\right) - \exp\left(-2\beta r_{N+1}^2\right)\right]$$

$$= 4\pi \sqrt{\beta} \left[\Gamma(3/2)\left(1 - \frac{1}{2\sqrt{2}}\right) + \frac{\Gamma(1/2)}{2}\left(\frac{1}{\sqrt{2}} - 1\right)\right]. \quad (53)$$

The potential matrix element V_{11} is

$$V_{11} = \sum_{i=1}^{N} \sum_{j=1}^{N} 4\pi b_i b_j \left(\frac{(2\pi)^N}{\det(B^i + B^j)}\right)^{\frac{3}{2}} \sum_{k=1}^{N} \int d^3 r$$

$$\times \left[1 - \exp\left(-\beta r_{N+1}^2\right)\right]^2 \text{erfc}\left(\sqrt{\frac{c_{ijk}}{2}} r_{N+1}\right). \quad (54)$$

The integration for V_{11} is done numerically using Gaussian quadratures. The $I_{10} = T_{10} + V_{10}$ matrix element has no kinetic energy term and is written as

$$
V_{10} = \int d\Omega_{N+1} \int dr_{N+1} \, r_{N+1}
$$
$$
\times \left[1 - \exp\left(-\beta r_{N+1}^2 \right) \right] V_{N+1}(\mathbf{r}_{N+1}) \tag{55}
$$
$$
= 4\pi \sum_{i=1} \sum_{j=1} b_i b_j \left(\frac{(2\pi)^N}{\det(B^i + B^j)} \right)^{\frac{3}{2}} \sum_{k=1}^{N} \left[\sqrt{\frac{2}{\pi \, c_{ijk}}} \right.
$$
$$
\left. - \int dr_{N+1} \exp\left(-\beta r_{N+1}^2 \right) \mathrm{erfc}\left(\sqrt{\frac{c_{ijk}}{2}} r_{N+1} \right) \right]. \tag{56}
$$

The potential energy term for V_{01} is the same as V_{10}. However, $T_{01} = \langle \Psi_0 | -\frac{\nabla_{N+1}^2}{2} | \Psi_1 \rangle$ is finite and

$$
I_{01} = \langle \Psi_1 | (H - \epsilon_0) | \Psi_0 \rangle + \langle \Psi_0 | -\frac{\nabla_{N+1}^2}{2} | \Psi_1 \rangle, \tag{57}
$$

where

$$
T_{01} = -\langle \Psi_0 | \frac{1}{r_{N+1}} \beta \left(1 - 2\beta r_{N+1}^2 \right)
$$
$$
\times \exp\left(-\beta r_{N+1}^2 \right) | \Phi_0 \rangle = 2\pi. \tag{58}
$$

The integrals I_{00}, I_{10}, and I_{11} only need to be evaluated just once at the beginning of any calculation.

The matrix element between two short-range functions is evaluated trivially since it is exactly the same as that used in bound-state calculations with the additional factor of E.

$$
I_{mn} = \langle \Psi_m | (H - \epsilon_0) | \Psi_n \rangle. \tag{59}
$$

Type I and II basis functions were computed with exactly the same procedures without taking into account that the electronic part of the type II basis functions are close to an eigenstate.

The next class of matrix elements are those involving one continuum function and one of the short-range correlation terms. There are two terms to consider. The first, involving Ψ_1, is

$$
I_{m1} = \langle \Psi_m | -\frac{\nabla_{N+1}^2}{2} \left(\frac{1}{r_{N+1}} \left[1 - \exp\left(-\beta r_{N+1}^2 \right) \right] \right) | \Phi_0 \rangle
$$
$$
+ \langle \Psi_m | \frac{Z}{r_{N+1}^2} \left[1 - \exp\left(-\beta r_{N+1}^2 \right) \right] | \Phi_0 \rangle
$$
$$
- \langle \Psi_m | \sum_{i=1}^{N} \frac{1}{r_{N+1,i}} \frac{1}{r_{N+1}} \left[1 - \exp\left(-\beta r_{N+1}^2 \right) \right] | \Phi_0 \rangle, \tag{60}
$$

and assumes that $H_{\mathrm{atom}} | \Phi_0 \rangle = \epsilon_0 | \Phi_0 \rangle$. The kinetic integral reduces to

$$
T_{m1} = -\langle \Psi_m | \frac{\beta}{r_{N+1}} \left(1 - 2\beta r_{N+1}^2 \right) \exp\left(-\beta r_{N+1}^2 \right) | \Phi_0 \rangle. \tag{61}
$$

Both the Gaussian factor and constant (this is treated as a Gaussian with exponent zero) can be absorbed into $| \Phi_0 \rangle$ and the resulting matrix elements are a standard type. This is also true for the second term. The third term in Eq. (60) requires integrals of the type,

$$
I = \langle G(P', N+1) | \frac{1}{r_{N+1,i}} \frac{1}{r_{N+1}}
$$
$$
\times \left[1 - \exp\left(-\beta r_{N+1}^2 \right) \right] | G(P, N) \rangle. \tag{62}
$$

One first integrates over the electron coordinates to give an expression resembling Eq. (50). Then it is possible to numerically integrate over the positron coordinate.

The final matrix element involving $|\Psi_0\rangle$ and $|\Psi_i\rangle$ is of a standard type since the positron wave function in $|\Psi_0\rangle$ can be replaced by a Gaussian with exponent zero.

2. Molecular systems

The matrix elements for molecules involve additional complications that require special attention. The integration with respect to the electrons coordinates are evaluated analytically. The electric potential produced by the target ground state is defined as

$$
V_{N+1}(\mathbf{r}_{N+1}) = \langle \Phi_0 | \sum_{i=1}^{N} \frac{1}{|\mathbf{r}_{N+1} - \mathbf{r}_i|} | \Phi_0 \rangle
$$
$$
+ \frac{1}{|\mathbf{r}_{N+1} - \mathbf{R}/2|} + \frac{1}{|\mathbf{r}_{N+1} + \mathbf{R}/2|}. \tag{63}
$$

The first term of $V_{N+1}(\mathbf{r}_{N+1})$ involving $\frac{1}{|\mathbf{r}_{N+1} - \mathbf{r}_k|}$ is in the form,

$$
V_{N+1}(\mathbf{r}_{N+1})
$$
$$
= \sum_{i=1} \sum_{j=1} b_i b_j \left(\frac{(2\pi)^N}{\det(B^i + B^j)} \right)^{\frac{3}{2}} \sum_{k=1}^{N} \frac{1}{s_k} \mathrm{erf}\left(\sqrt{\frac{c_{ijk}}{2}} s_k \right), \tag{64}
$$

where $s_k = |((B^i + B^j)^{-1}(B_i \mathbf{s}_i + B_j \mathbf{s}_j))_k - \mathbf{r}_{N+1}|$ and $\mathbf{s}$ is defined in Eq. (17). Its second and third terms are trivial. This potential $V_{N+1}(\mathbf{r}_{N+1})$ is obviously dependent on both radius r_{N+1} and polar angle θ.

As in the atomic case, the matrix element I_{00} does not involve a contribution from the kinetic energy, so

$$
I_{00} = \langle \Psi_0 | (H - \epsilon_0) | \Psi_0 \rangle = \int d^3 r_{N+1} \, V_{N+1}(\mathbf{r}_{N+1}). \tag{65}
$$

The matrix elements of $V_{N+1}(\mathbf{r}_{N+1})$ are computed numerically using Gaussian quadratures on a two-dimensional spherical polar integration grid. The angular integration variable is θ. Special care is taken to remove the singularity at the nuclear centers since these can lead to inaccuracies. The following identity,

$$
\int d^3 r \, \frac{X(\mathbf{r})}{|\mathbf{r} - \mathbf{R}_0|}
$$
$$
= \int d^3 r \, \frac{X(\mathbf{r}) - X(\mathbf{R}_0) \exp[-\beta(\mathbf{r} - \mathbf{R}_0)^2]}{|\mathbf{r} - \mathbf{R}_0|} + \frac{2\pi X(\mathbf{R}_0)}{\beta}, \tag{66}
$$

can be used to eliminate the singularity from the numerical quadrature. The integral over the azimuthal angle is trivial and leads to a factor of 2π. Generally, $X(\mathbf{r})$ is in the form $X(\mathbf{r}) = r^n \exp(-ar^2 + br_z)$ with $-2 \leqslant n \leqslant 0$ and $a > 0$. The value chosen for β must be large enough for $X(\mathbf{R}_0) \exp[-\beta(\mathbf{r} - \mathbf{R}_0)^2]$ to approach $X(\mathbf{R}_0)$ faster than $X(\mathbf{r})$ when $\mathbf{r} \to \mathbf{R}_0$. Typically, we choose $\beta = a + 2.1$.

The kinetic energy matrix elements of I_{00}, I_{10}, and I_{11} are computed in exactly the same way as the atomic case. The potential energy matrix elements are evaluated numerically.

There are two types of short-range basis functions with the following matrix elements:

$$I_{m\mathrm{II}n\mathrm{II}} = \langle \Psi_m^{\mathrm{II}} | H_{N+1} | \Psi_n^{\mathrm{II}} \rangle, \tag{67}$$

$$I_{m\mathrm{II}n\mathrm{I}} = \langle \Psi_m^{\mathrm{II}} | H_{N+1} | \Psi_n^{\mathrm{I}} \rangle, \tag{68}$$

$$I_{m\mathrm{I}n\mathrm{I}} = \langle \Psi_m^{\mathrm{I}} | (H - \epsilon_0) | \Psi_n^{\mathrm{I}} \rangle. \tag{69}$$

The kinetic energy part of $I_{m\mathrm{II}n\mathrm{II}}$ is easy to compute analytically since the positron wave function is effectively decoupled from the electron wave function. The potential energy integrals over $V_{N+1}(\mathbf{r}_{N+1})$ are done numerically to avoid the double sums over the ECGs comprising $|\Phi_0\rangle$. All the integrals involved in $I_{m\mathrm{II}n\mathrm{II}}$ and $I_{m\mathrm{I}n\mathrm{I}}$ are done analytically with the usual expressions for ECG matrix elements.

The next class of matrix elements involves one short-range and one long-range basis function. Using $H_{\mathrm{molec}}|\Phi_0\rangle = \epsilon_0|\Phi_0\rangle$ gives

$$I_{m\mathrm{II}0} = \langle \Psi_m^{\mathrm{II}} | H_{N+1} | \Psi_0 \rangle, \tag{70}$$

$$I_{m\mathrm{I}0} = \langle \Psi_m^{\mathrm{I}} | H_{N+1} | \Psi_0 \rangle, \tag{71}$$

$$I_{m\mathrm{II}1} = \langle \Psi_m^{\mathrm{II}} | H_{N+1} | \Psi_1 \rangle, \tag{72}$$

$$I_{m\mathrm{I}1} = \langle \Psi_m^{\mathrm{I}} | H_{N+1} | \Psi_1 \rangle. \tag{73}$$

The $I_{m\mathrm{I}0}$ matrix element is reduced to a standard $N+1$ particle matrix element by writing the positron orbital in Ψ_0 as a Gaussian with an exponent of zero. The kinetic energy matrix element for $I_{m\mathrm{II}0}$ is zero. The potential energy matrix element for $I_{m\mathrm{II}0}$ is evaluated by a numerical integration over the $V_{N+1}(\mathbf{r}_{N+1})$ of Eq. (63).

The $I_{m\mathrm{II}1}$ potential energy matrix elements are computed by a numerical quadrature over $V_{N+1}(\mathbf{r}_{N+1})$. The kinetic energy matrix elements of $I_{m\mathrm{II}1}$ were evaluated by a Gaussian quadrature after operating with ∇^2 on the positron orbital.

The $I_{m\mathrm{I}1}$ matrix elements are the most complicated. The ∇^2 first operates on the positron orbital of $|\Psi_1\rangle$. Once this is done, the resulting integrals can be recast into the form $\langle G(P',\mathbf{s}')||\mathbf{r}_i|^\alpha|G(P,\mathbf{s})\rangle$, which is a type of integration similar to Eq. (42). For the positron nucleus potential energy matrix elements of $I_{m\mathrm{I}1}$ one first integrates over the electron coordinates. The resulting function, which is in the form of $\exp(-ar^2 + \mathbf{r} \cdot \mathbf{d})/|\mathbf{r} \pm \mathbf{R}_0|$, where $\mathbf{d}$ lies along the internuclear axis, is integrated numerically over the positron coordinate with the singularities handled using Eq. (66). The electron-positron matrix elements of $I_{m\mathrm{I}1}$ are evaluated by first integrating over the electron coordinates. The resulting numerical two-dimensional integration over the positron coordinate is straightforward since there the Coulomb singularity is situated at the origin of the positron coordinate system.

G. Positron annihilation

The annihilation parameter Z_{eff} is computed from the scattering wave function using the identity [23–25],

$$Z_{\mathrm{eff}} = \langle \Psi_t | \sum_{i=1}^{N} \delta(\mathbf{r}_{N+1} - \mathbf{r}_i) | \Psi_t \rangle. \tag{74}$$

This expression has been written down after the spin projection and spin averaging. In the plane-wave Born approximation, the wave function is written as the product of the ground state and a plane wave for the positron, and Z_{eff} is equal to the number of electrons.

The annihilation parameter requires the evaluation of the matrix element of the interparticle δ function. The matrix elements involving the continuum positron orbitals are

$$Z_{0,0} = N\langle \Phi_0 | \Phi_0 \rangle = N, \tag{75}$$

$$Z_{1,0} = \langle \Phi_0 | \sum_{i=1}^{N} \frac{1}{r_i} [1 - \exp(-\beta r_i^2)] | \Phi_0 \rangle, \tag{76}$$

$$Z_{1,1} = \langle \Phi_0 | \sum_{i=1}^{N} \frac{1}{r_i^2} [1 - \exp(-\beta r_i^2)]^2 | \Phi_0 \rangle. \tag{77}$$

All the other classes of matrix elements involve the use of ECGs to represent the positron. In the case of positron-atom systems, all other matrix elements can be calculated analytically. In the case of molecules, matrix elements involving type II basis functions and/or continuum orbitals (e.g., $Z_{m\mathrm{II},n\mathrm{II}}$, $Z_{m\mathrm{II},0}$, $Z_{m\mathrm{II},1}$) reduce to two-dimensional integrals similar to Eqs. (75)–(77).

All matrix elements involving at least one type I ECG are done analytically. For example, consider $Z_{m\mathrm{I},1}$ which involves a type I ECG with a continuum orbital. This is

$$Z_{m\mathrm{I},1} = \langle \Psi_m^{\mathrm{I}} | \sum_{i=1}^{N} \delta(\mathbf{r}_{N+1} - \mathbf{r}_i) \frac{(1 - \exp(-\beta r_{N+1}^2))}{r_{N+1}} | \Phi_0 \rangle. \tag{78}$$

Upon integrating over the positron coordinate, this can be written

$$Z_{m\mathrm{I},1} = \sum_{i=1}^{N} \langle \Omega_{m,i}^{\mathrm{I}} | \frac{[1 - \exp(-\beta r_i^2)]}{r_i} | \Phi_0 \rangle, \tag{79}$$

where $\Omega_{m,i}^{\mathrm{I}}$ is an ECG obtained by converting the positron coordinate in Ψ_m^{I} to that of electron i.

1. Consideration of the internuclear distance

It is quite common in previous work for Z_{eff} to be computed at an internuclear separation of $R = 1.4.0a_0$ since this represents the minimum in the H_2 potential curve. However, this does not take the shape of the H_2 nuclear wave function into consideration and the preferred internuclear distance for a comparison with experiment is at the mean distance of the H_2 vibrational wave function.

In the Born-Oppenheimer approximation the scattering length and Z_{eff} can be treated as parametric functions of R [i.e., $Z_{\mathrm{eff}} = Z_{\mathrm{eff}}(R)$]. The actual values of Z_{eff} to be compared

with experiment, should be

$$\langle Z_{\text{eff}} \rangle = \int |\Psi_{\text{vib}}(R)|^2 Z_{\text{eff}}(R) \, dR. \qquad (80)$$

Now expand $Z_{\text{eff}}(R)$ in a Taylor series about the mean radius, R_0 of the H$_2$ vibrational ground state, that is,

$$Z_{\text{eff}}(R) \approx Z_{\text{eff}}(R_0) + (R - R_0)\left(\frac{dZ_{\text{eff}}}{dR}\right)_{R=R_0} + \cdots. \qquad (81)$$

Substituting this expression into Eq. (80). The integral to first-order variations about R_0 reduces to

$$\langle Z_{\text{eff}} \rangle \approx Z_{\text{eff}}(R_0) + \left(\frac{dZ_{\text{eff}}}{dR}\right)_{R=R_0} \int |\Psi_{\text{vib}}(R)|^2 (R - R_0) \, dR. \qquad (82)$$

The remaining integral is zero, and therefore $\langle Z_{\text{eff}} \rangle$ can be equated with its parametric value at the mean internuclear radius.

III. THE SCATTERING OF POSITRONS FROM ATOMIC HYDROGEN

Calculations on the positron-hydrogen system can be used to validate the present methodologies since there have been a number of sophisticated calculations of this system [14,27–29]. The inner basis used in the variational calculations came from a CVM calculation. The parameters for the confining potential were $\lambda = 1.3589904 \times 10^{-4}$ and $R_0 = 18.0\,a_0$. The inner basis consisted of a total of 400 ECGs and the number of states for which the energy was optimized was two.

The Kohn variational calculation used these 400 inner basis functions plus another 35 type II basis functions formed by multiplying the H ground state by a simple Gaussian for the positron. The positron Gaussians were generated by the rule $\alpha_i = \alpha_1 / T^{i-1}$ where α_1 was 526.684 and $T = 1.435$. The smallest exponent of this set was 2.44673×10^{-3}.

The hydrogen ground state was represented by a set of energy-optimized ECGs (in this case they collapse to ordinary Gaussians). Table I lists the energy of the hydrogen ground state as a function of the number of Gaussians. The cutoff parameter β in $|\Psi_1\rangle$ was $2.10\,a_0^{-2}$.

Table II lists the scattering length and Z_{eff} for different calculations using ECG expansions of varying length to represent the confined e^+H system and the H ground state. The relatively small degree of variation in the scattering

TABLE I. Convergence of the energy (in a.u.) for H and He as a function of the dimensionality of the numbers of ECG basis (N).

H		He	
N	E	N	E
10	−0.4999993182	50	−2.903722945661
15	−0.4999999723951	60	−2.903723953521
20	−0.4999999994272	80	−2.903724303851
24	−0.4999999999151	90	−2.903724330121
26	−0.4999999999721	100	−2.903724348174
		120	−2.903724363908
Exact	−0.50000000000000	Exact [26]	−2.903724377034

TABLE II. The convergence of the scattering length and zero energy annihilation parameter as a function of the number of ECGs in the representation of the hydrogen ground state and in the energy optimized inner basis. Calculations by other groups are also listed.

N_{H}	N_{inner}	A	Z_{eff}
10	435	−2.0522	8.8649
15	435	−2.0523	8.8651
20	235	−2.0368	8.8288
20	285	−2.0442	8.8041
20	335	−2.0412	8.8366
20	385	−2.0463	8.8624
20	435	−2.0525	8.8651
CI-Kohn [29]		−2.088	8.565
SVM-stabilization [14]		−2.094	8.75
Variational [27,28]		−2.104	8.868

length when the dimension of the hydrogen ground state was increased from 10 to 20 indicates the scattering parameters are insensitive to the approximate nature of the hydrogen wave function at the current level of precision.

The scattering length function did not decrease monotonically with increasing basis set size. No rigorous principle applies here since the wave function with smaller dimension basis sets are *not* subsets of the larger dimension basis sets.

The scattering length would seem to be about 2% different from the best estimate. This is not unexpected since no basis functions are included to represent the impact of target polarization on the positron at long range. Such functions are known to be important in getting an accurate value for the scattering length [27,30]. This problem did not impact the SVM-stabilization estimate of the scattering length (using a similar short-range basis) since the long-range polarization potential was included when fitting the wave function and computing phase shifts [14].

No such discrepancy exists for Z_{eff}. The ECG basis set does a very good job of describing the short-range correlations that are so important in the annihilation process.

IV. THE SCATTERING OF POSITRONS FROM ATOMIC HELIUM

Some of the best calculations of low-energy positron scattering from helium come from the Kohn variational calculations of Humberston and coworkers at the University College London (UCL) [31–33]. Another high-quality calculation was the SVM-stabilization calculation [14] which gave a scattering length and Z_{eff} that were compatible with the UCL values.

The inner basis used in the variational calculations came from a calculation using the CVM. The parameters for the confining potential were $\lambda = 1.175520 \times 10^{-4}$ and $R_0 = 17.0\,a_0$. The inner basis consisted of a total of 1600 ECGs and the number of states used in the energy optimization was two. The type II basis functions were constructed by multiplying an ECG representation of the He ground state with an even-tempered Gaussian basis set. The positron Gaussians were generated by the rule $\alpha_i = \alpha_1 / T^{i-1}$ where α_1 was 526.684 and $T = 1.435$. Table I lists the energy of the helium ground state

TABLE III. The convergence of the scattering length and zero energy annihilation parameter as a function of the number of ECGs in the representation of the helium ground state and in the energy optimized inner basis. Calculations by other groups are also listed.

N_{He}	N_{inner}	A	Z_{eff}
60	1035	−0.449522	3.975779
80	1035	−0.449541	3.975797
100	1035	−0.449543	3.975800
80	1235	−0.451354	3.980779
80	1435	−0.451929	3.988951
80	1635	−0.452138	3.991765
Variational: UCL [32]		−0.50	3.932
SVM-stabilization [14]		−0.474	3.955
Experiment, $k \approx 0.045\, a_0^{-1}$ [40]			3.89 ± 0.04
Experiment, $k \approx 0.045\, a_0^{-1}$ [41]			3.94 ± 0.02
Experiment, $k \approx 0.045\, a_0^{-1}$ [42]			3.86 ± 0.04

as a function of the number of ECGs. The cutoff parameter β in $|\Psi_1\rangle$ was $2.10\, a_0^{-2}$.

Table III lists the scattering length and Z_{eff} for different calculations using ECG expansions of varying length to represent the confined e^+He system and the He ground state. The impacts of using approximate target wave functions in variational calculations of positron scattering from He or H$_2$ has been a topic of constant concern [31,34–39] over a long period of time. One typically has to compromise either the accuracy of the target wave function or the accuracy of the scattering wave function. This issue did not manifest itself the present calculations. The variation in the scattering length when the dimension of the He basis was increased from 60 to 100 was only $2 \times 10^{-6}\, a_0$. The advantage of the ECG basis is that it is straightforward to generate target wave functions of sufficient precision to effectively eliminate errors associated with the use of an approximate wave function.

The present scattering length of $-0.452\, a_0$ is slightly less negative than the stabilization-SVM estimate $-0.474\, a_0$ and the previous Kohn variational estimate by the UCL group of $-0.50\, a_0$. There is some uncertainty attached to the UCL scattering length since this was not directly computed by the Kohn group. Rather, the low-energy $k = 0.1$ and $k = 0.2\, a_0^{-1}$ phase shifts were used to tune a model potential which was then used to determine the scattering length.

The current value of Z_{eff} is about 1%–2% larger than previous calculations. The value of Z_{eff} tended to increase in size as the dimension of the short-range basis increased in size. This tendency is something that also happens to positron annihilation rates in SVM calculations of exotic positron binding atoms and ions. The UCL Kohn variational Z_{eff} was taken from a polynomial fit to calculated values. It should be noted that this polynomial fit had a term linear in k [32], but effective range theory suggests that such a term is not possible [43].

Comparison with experiment relies on an estimate of the change in Z_{eff} with k as the momentum is increased to $0.045\, a_0^{-1}$. The semiempirical method of Mitroy and Ivanov [44] was applied and this gave an estimate of 3.942 at this momentum. The contribution to Z_{eff} due to p-wave

scattering using the method of [44] was only 0.0050. The present calculation of Z_{eff} is compatible with the experimental values given the spread in experiment [40–42].

V. THE SCATTERING OF POSITRONS FROM MOLECULAR HYDROGEN

There have been a number of calculations of low-energy e^+-H$_2$ scattering and annihilation [17,39,50–54]. At present, all previous calculations with one exception [17] significantly underestimate the experimental low-energy annihilation cross section. The calculation by Zhang *et al.* [17] can be regarded as a direct precursor to the present work. One of the more startling aspects of the Zhang *et al.* calculation was the prediction of a virtual state with a scattering length of $-13\, a_0$ at an internuclear separation of $R \approx 3.0\, a_0$. Prior to this, the most sophisticated calculations were the Kohn variational calculations performed by Armour and colleagues at the University of Nottingham (UN) [39,51,54,55].

A. The target wave function

Table IV lists the properties of the H$_2$ ground-state wave function as a function of internuclear distance. The dimension of the ECG basis used in these calculations was 120. In no instance are the differences between the present ground-state energies and the best correlated energies larger than 10^{-5} a.u. Comparisons are also made with other calculations of the quadrupole moment.

A basis of dimension of 120 gave an energy of -1.17447554 a.u. at $R = 1.40\, a_0$. The best H$_2$ energy at an internuclear separation of $1.40\, a_0$ is -1.17447571 a.u. [48]. Our wave function recovers 99.996% of the correlation energy of 0.04084 a.u. [56].

A noticeable feature is the maxima in both the quadrupole moment and the polarizability for R between 3 and $4\, a_0$. The table lists the scalar (α_d) and tensor (γ_d) polarizabilities. The polarizability at an angle of θ with respect to the internuclear axis is

$$\alpha(\theta) = \alpha_d + \gamma_d P_2(\cos\theta), \tag{83}$$

where P_2 is a Legendre polynomial. The polarizability is tabulated for reasons that will become evident later.

B. The static model

In the static model, the wave function for the H$_2$ ground state is treated as inert and the trial wave function consists of simple products of positron orbitals multiplying the H$_2$ ground-state wave function.

There were two classes of type II basis functions used to represent the interaction of the positron with the H$_2$ target. The first were functions given by Eq. (18). The α_k were an even-tempered set given by the identity $\alpha_j = \alpha_1/T^{j-1}$ with $\alpha_1 = 526.684$ and $T = 1.435$. A total of 35 functions of this type were added to interaction region basis. However, an additional 15 molecular type II functions given by Eq. (19) were included. The α_k were an even-tempered set given by the identity $\alpha_j = \alpha_1/T^{j-1}$ with $\alpha_1 = 56.6685$ and $T = 1.435$. The vector **s** was on the internuclear axis and for $R = 1.40\, a_0$ was set to lie $0.68\, a_0$

TABLE IV. Energies, quadrupole moments and polarizabilities of the H_2 molecule at different inter-nuclear separations. The dimension of the ECG basis used in the present SVM calculations was 120.

R	E	E_{SVM}	Q [45]	Q_{SVM}	α_d [46,47]	γ_d [46]
1.00	−1.12453968 [18]	−1.12453940	0.5130798	0.51269	3.5900	0.7468
1.20	−1.16493520 [18]	−1.16493504	0.7060458	0.70547	4.3448	1.2026
1.40	−1.17447571 [48]	−1.17447554	0.9136887	0.91291	5.1786	1.8028
1.45	−1.17405704 [18]	−1.17405678		0.96612	5.3981	1.9763
1.60	−1.16858334 [18]	−1.16858314	1.1280073	1.12699	6.0786	2.5531
1.80	−1.15506870 [18]	−1.15506841	1.3402226	1.33893	7.0255	3.4425
2.00	−1.13813292 [18]	−1.13813261	1.5408174	1.53924	7.9954	4.4535
2.20	−1.12013208 [18]	−1.12013157	1.7197200	1.71795	8.9523	5.5280
2.40	−1.10242257 [18]	−1.10242202	1.8645725	1.86473	9.8568	6.6000
2.60	−1.08579120 [18]	−1.08579040	1.9702597	1.97042	10.6649	7.5874
3.00	−1.05732624 [18]	−1.05732583	2.0300798	2.02975	11.8263	8.9202
3.40	−1.03607537 [18]	−1.03607484	1.8776539	1.87755	12.2281	9.0159
3.80	−1.02154973 [49]				11.9599	7.9345
4.00	−1.01639020 [49]	−1.01638972	1.3812208	1.38124	11.6697	7.1230
5.00	−1.00378563 [49]				9.4183	2.5650
6.00	−1.00083568 [49]	−1.00083510		0.19032	8.9348	1.1248
7.00	−1.00019787 [49]				8.7758	0.5683
7.20	−1.00015095 [49]	−1.00015053		0.045953		

away from the internuclear center. This vector was usually chosen to be a distance of $(R/2 - 0.02 a_0)$ from the center of the internuclear axis for other internuclear separations.

There were no extensive optimizations for the static model calculations and the accuracy of the scattering length and Z_{eff} can be estimated as being of the order of 0.1%–0.5%. The scattering length at $R = 1.40 a_0$ was about $0.6855 a_0$ while Z_{eff} was 0.624.

C. Full variational calculations

The CVM calculations to construct the type I inner basis optimized the energies of the two lowest eigenstates. The parameters for the confining potential were $\lambda = 1.175520 \times 10^{-4}$ and $R_0 = 17.0 a_0$.

Table V shows the convergence of the scattering length and Z_{eff} for various size basis sets. The first issue to be addressed is whether the results showed any significant change with respect to the variation of the H_2 target wave function itself. The changes in Z_{eff} when the dimension of the H_2 wave function was increased from 60 to 120 were restricted to the fifth digit. The immediate conclusion is that it is safe to use H_2 wave functions of dimension 100 and this was mostly done in Table VI where the scattering parameters are studied as a function of internuclear separation. The difference between the first-order scattering length (i.e., A_t) and A for the biggest calculation using the basis of dimension 1049 was about 0.5% with $A_t = -2.554 a_0$.

The variation of the scattering parameters with respect to the increase in the inner basis dimension is also listed in Table V. There were typically 50 type II basis functions for each calculation. The dimension of the largest calculation included 999 type I inner basis functions. Some of the time the stochastic optimization resulted in basis functions with the large exponents exceeding 1000, multiplying the positron coordinate in Eq. (17). This led to severe inaccuracies in the

evaluation of the I_{mI1} matrix element. The simplest way to solve the problem was to selectively omit basis functions with excessively large positron exponents from the Kohn calculation.

The current Kohn variational scattering length is compatible with the estimates of our previous CVM-stabilization calculation [17]. The largest calculation at $R = 1.40 a_0$ gave a value of Z_{eff} of 14.60. Experiments give values of 14.7(2) [58], 14.61(14) [59], and 16.02(08) [60]. It has been suggested that the variation between the different values is related to whether the positrons are thermalized when the annihilation spectrum is measured [60]. Even though it is common to report scattering parameters at $R = 1.40 a_0$, and this was done in Table V, comparison with experiment is best done by evaluating Z_{eff} at the mean internuclear separation of the H_2 ground vibrational state, namely $1.4487 a_0$ [10]. The present calculation gives $Z_{eff} = 15.70$ at $R = 1.45 a_0$. This favors the slightly larger experimental Z_{eff} of 16.02(08) [60].

The Kohn calculations give the zero-energy Z_{eff} and direct comparison with experiment requires an estimate of the annihilation at thermal energies. A rough estimate of the thermal energy Z_{eff} can be made by using an approximate formula [61], for example,

$$Z_{eff}(k) \approx \frac{Z_{eff}(k = 0)}{1 + (A_{scat}k)^2}. \tag{84}$$

Application of this result with a scattering length of $-2.7 a_0$ suggests a 1.5% reduction in the annihilation parameter at thermal energies to a value of 15.5.

Apart from the precursor to the present calculation [17], the most sophisticated calculations by another group are the Kohn variational calculations by Armour and colleagues at the University of Nottingham (UN) [39,51,54,55]. Table V gives some representative results from calculations by the UN group. Kohn calculations can be performed within two

TABLE V. The convergence of the scattering length and zero energy annihilation parameter for positron scattering from the H_2 molecule in the fixed nuclei approximation at an inter-nuclear separation of $1.40\,a_0$. The number of ECGs in the representation of the H_2 state and in the energy optimized inner basis are listed. Results of calculations by other groups are included.

N_{H_2}	N_{inner}	A	Z_{eff}
60	850	-2.55590	14.6385
80	850	-2.55591	14.6399
100	850	-2.55593	14.6403
120	850	-2.55596	14.6407
100	450	-2.4547	13.1041
100	650	-2.5427	14.3709
100	850	-2.5593	14.6407
100	1049	-2.5648	14.6065
CVM/stabilization: [17]		-2.56	14.8
Kohn: Method of models, (1986) [51]		-2.2	10.3
Kohn: $k = 0.04\,a_0^{-1}$ [39,55]			≈ 9.6
Kohn: Method of models, $k = 0.04\,a_0^{-1}$ [39,55]			≈ 12.6
Kohn: Method of models, $k = 0.01\,a_0^{-1}$ [57]		-2.56	≈ 13.5

different theoretical frameworks (i.e., one set comes from a standard Kohn calculation and the other is computed within the framework of the method of models). Table V shows significant differences between recent calculations by the UN group [39,55] using these two methodologies. For example, the strong variation of Z_{eff} with R at $R = 1.4\,a_0$ is absent in the UN Kohn variation without the method of models [55]. The UN method of models Z_{eff} does increase with increasing R [55], but the rate of increase is less than half the size of the present $Z_{eff}(R)$. For a variety of reasons, one being the differences between calculations with and without using the method of models, there had been some uncertainty about the reliability of calculations undertaken using the method of models [55]. However, examination of variationally optimized results taken from the thesis of Cooper [62] reveals a scattering length of $-2.56\,a_0$ and a Z_{eff} of 13.5 that are quite close to the present Kohn values. It appears that the UN method of models calculations were starting to give a reasonable description of the scattering dynamics although further increases in the size of this calculation are desirable.

The $R = 1.45\,a_0$ scattering length of $-2.709\,a_0$ implies a zero-energy cross section of $\sigma(0) \approx 29.3\,\pi a_0^2$. A recent experiment by the Trento group [63] had a cross section of $8.3\,\pi a_0^2$ at $k \approx 0.086\,a_0^{-1}$. The very small experimental cross section is incompatible with the present zero-energy cross section. Improving the quality of the Kohn calculation would only lead to the magnitude of the scattering length increasing, and thus result in even larger discrepancies with the Trento cross section [63]. One important class of functions would be those that include the effect of target polarization on the positron at large distances from the target [64].

D. Variation with internuclear distance

One of the more interesting aspects of the zero-energy collision dynamics is the variation in the scattering dynamics as a function of internuclear separation. Table VI shows the static model exhibiting relatively little variation with R. Most of the values of the full calculation in Table VI lie within 1%–2% of numerical values computed with the CVM-stabilization

TABLE VI. The scattering length A and Z_{eff} for the static model and the full variational calculation for zero energy e^+-H_2 scattering. The number of short-range basis functions for the full calculation was about 850 (or more) for almost all of the values reported.

	static model		full calculation	
R	A	Z_{eff}	A_s	Z_{eff}
0.00	0.4284	0.6860		
0.20	0.4476	0.6761		
0.40	0.4854	0.6599		
0.60	0.5283	0.6457	-0.876	5.754
0.80	0.5715	0.6352		
1.00	0.6127	0.6283	-1.522	8.798
1.10	0.6344	0.6224		
1.20	0.6510	0.6248	-1.982	11.23
1.30	0.6688	0.6241	-2.271	12.84
1.40	0.6855	0.6242	-2.565	14.61
1.45	0.6943	0.6240	-2.709	15.70
1.50	0.7015	0.6247	-2.900	16.81
1.60	0.7165	0.6259	-3.233	19.41
1.80	0.7434	0.6295	-4.102	25.91
2.00	0.7663	0.6346	-5.202	35.24
2.20	0.7899	0.6370	-6.392	47.63
2.40	0.8050	0.6466	-7.867	65.48
2.60	0.8211	0.6525		
2.80	0.8365	0.6577	-10.97	111.6
3.00	0.8517	0.6617	-12.35	134.4
3.20	0.8674	0.6645	-13.09	150.1
3.40	0.8838	0.6660	-13.18	151.3
3.60	0.9009	0.6665	-12.79	142.2
4.00	0.9471	0.6601	-10.72	107.8
4.40	0.9677	0.6659	-8.911	76.82
4.80	0.9951	0.6673	-7.522	57.77
5.20	1.0172	0.6703	-6.616	46.42
5.60	1.0346	0.6748	-5.996	40.17
6.00	1.0482	0.6799	-5.602	35.04
6.40	1.0589	0.6853		
6.80	1.0686	0.6925		
7.20	1.0740	0.6960		

approach [17]. At $R = 0\,a_0$, the values of A and $Z_{\rm eff}$ should be the same as those of the static model calculation for helium, and this is indeed the case. The $Z_{\rm eff}$ decreases as the internuclear distance increases until $R = 1.3\,a_0$. Further increase in R leads to $Z_{\rm eff}$ increasing. But the overall variation in $Z_{\rm eff}$ as the internuclear distance changes from 0 to $7.2\,a_0$ was about 10%. The R dependence of A exhibits more variation, with a 250% increase occurring from $R = 0$ to $R = 7.2\,a_0$.

The second-order derivative $\frac{d^2 Z_{\rm eff}}{dR^2}$ is positive near the mean internuclear nuclear distance of $1.45\,a_0$ which means that second-order correction to Eq. (82) would result in $\langle Z_{\rm eff} \rangle$ increasing. The second-order correction to Eq. (82) would be

$$
\begin{aligned}
\delta \langle Z_{\rm eff} \rangle &\approx \left(\frac{1}{2} \frac{d^2 Z_{\rm eff}}{dR^2} \right)_{R=R_0} \int |\Psi_{\rm vib}(R)|^2 (R - R_0)^2 dR \\
&\approx \left(\frac{1}{2} \frac{d^2 Z_{\rm eff}}{dR^2} \right)_{R=R_0} \left(\langle R^2 \rangle - R_0^2 \right).
\end{aligned}
\tag{85}
$$

Using the data of Table VI we estimate a value of $40\,a_0^{-2}$ for the second derivative. Using $\langle R \rangle = 1.448738\,a_0$ and $\langle R^2 \rangle = 2.127046\,a_0^2$ [10] for the H_2 ground-state vibrational wave function results in $\delta \langle Z_{\rm eff} \rangle \approx 0.6$. This corresponds to an increase of 4% and is largely due to the large size of the second derivative of $Z_{\rm eff}(R)$. This suggests a zero-energy $\langle Z_{\rm eff} \rangle$ for the ground-state vibrational wave function of about 16.3. Doing the same calculation, but correcting for the influence of finite energy using Eq. (84) leads to a correction of $\delta \langle Z_{\rm eff} \rangle \approx 0.5$. This further suggests that the $\langle Z_{\rm eff} \rangle$ for the ground vibrational state at thermal energies should be 16.0. The earlier analysis should be regarded as an approximate analysis aimed at getting reasonable estimates of corrections due to finite energies and internuclear separation effects. Calculations by the UN group using a Morse function for the H_2 vibrational wave function give $\langle Z_{\rm eff} \rangle = 13.5$ [55] for a trial wave function that gives the $Z_{\rm eff} = 12.6$ at $R = 1.4\,a_0$.

The mean internuclear distance for the deuterium molecule D_2 is $\langle R \rangle = 1.434562\,a_0$ [65]. This is $0.014\,a_0$ smaller than that of H_2. A quick linear interpolation suggests that the D_2 $Z_{\rm eff}$ should be about 0.3 smaller than the H_2 $Z_{\rm eff}$. At present, the available experimental measurements find no discernible difference between the H_2 and D_2 $Z_{\rm eff}$ [66].

The behavior of the static calculation scattering length invalidates a suggestion originally put forward to explain the existence of a virtual state at $R \approx 3.4\,a_0$ [17]. The critical value for a point quadrupole to bind a positron (or electron) is $2.4\,ea_0^2$ [67]. This is only 20% larger than the H_2 quadrupole moment at $R = 3.0\,a_0$. So it had been suggested that the virtual state owed its existence to the quadrupole moment of the H_2 ground state [17]. This is clearly not supported by the existing calculations in the static model.

At $R = 0$, the static model results are very close to the scattering length (0.425) and $Z_{\rm eff}$ (0.689) obtained by a direct numerical integration of the Schrödinger equation for positron scattering from the helium ground state. The zero-energy $Z_{\rm eff}$ and scattering length for the hydrogen ground state are 0.406 and $0.582\,a_0$, respectively.

The full variational Kohn scattering length tabulated in Table VI varies surprisingly quickly with R. The e^+-H_2 interaction is quite attractive with values lower than $-10\,a_0$

occurring for R between 2.8 and $4.0\,a_0$. The maximum in the polarizability at $3.4\,a_0$ (Table IV) seems to offer the more plausible explanation for the existence of the virtual state. Previous calculations with a model alkali-metal atom revealed binding for a critical polarizability of $23.5\,a_0^3$ [68] and the angle-averaged polarizability at $R = 3.4\,a_0$, $12.23\,a_0^3$ is more than twice as large as the H_2 polarizability at $R = 1.45\,a_0$, namely $5.40\,a_0^3$. The peak in A near $R \approx 3.3\,a_0$ also leads to a peak in $Z_{\rm eff}$. This is expected since large scattering lengths inevitably lead to a large threshold $Z_{\rm eff}$ [44,61,69].

The effective scattering length for the H_2 vibrational ground state can be estimated using a procedure similar to that used for $Z_{\rm eff}$. The second-order derivative, $\frac{d^2 A}{dR^2}$ is about -1.95 at $R = 1.45\,a_0$. The estimated correction to the scattering length of $-0.027\,a_0$ is about 1% giving a value of -2.736. The increase in the threshold cross section would be about 2%.

VI. CONCLUSIONS

The scattering lengths for positron scattering from H, He and the H_2 molecule have been determined with a Kohn variational calculation based on the usage of ECGs to represent the wave function in the interaction region. The interaction region basis was optimized by putting a confining potential around the target and treating the positron-target system as a bound state. One notable departure from previous variational calculations is that problems relating to the use of approximate target wave functions [31,34–39] are simply not an issue.

The main deficiency in the determination of the scattering length is probably the lack of basis functions to specifically model the long distance polarization interaction between the positron and the target. This results in the present scattering lengths for H and He overestimating the best estimates of the scattering length by about $0.05\,a_0$. Such an omission is not that important at present for the positron-H_2 system as it is the one of first treatments of this system with an unrestricted treatment of the positron-electron interactions. The present results use essentially the same interaction region wave functions as our previous work [17] (but with some improvements resulting from increased computation), but they have a firmer foundation since they were obtained using a method well known in scattering theory. Ad hoc procedures were used in Ref. [17] to extract scattering parameters from the interaction region wave functions.

The obvious improvements that could be made would be a better description of the long-range polarization interaction and the generalization of the current Kohn method to finite energies. There are no fundamental limitations to accomplishing either of these. Polarization interactions could be included by adding to the basis a polarized pseudostate (represented as a linear combination of ECGs) multiplying an even-tempered set of positron orbitals. There is also no impediment to performing finite energy calculations since many of the crucial integrals involving the positron projectile could be performed numerically after integrating over electron coordinates.

The extension of the present Kohn methodology to electron scattering is at yet uncertain. The exchange interaction between the target and projectile in this case would result in a new class of multidimensional integrals that need to be evaluated.

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