The importance of an accurate target wavefunction in variational calculations for (e⁺–H₂) scattering

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Abstract

Using the complex Kohn method, we have calculated variational values of phase shifts and the annihilation parameter, Zeff, for the elastic scattering of positrons by molecular hydrogen. Our results are sensitive to small changes in the accuracy of the wavefunction representing the target hydrogen molecule. We have developed a systematic approach to demonstrate that, at low positron energies, there are particular forms of the Kohn trial wavefunction for which the results of variational calculations are not reliable, even when the target wavefunction accounts for as much as 96.8% of the correlation energy of H₂. We find that reliable results can be recovered if our calculations are extended to admit more sophisticated target wavefunctions accounting for 99.7% of the correlation energy. Remaining discrepancies between theory and experiment are briefly discussed.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

In a previous article [1], preliminary calculations of phase shifts were presented for the elastic scattering of low energy positrons by molecular hydrogen. The calculations used a generalized form of the Kohn variational method [2] and were carried out for the lowest partial wave of Σ⁺₁ symmetry, which has been shown [3] to be the only significant contributor to scattering processes for incident positron energies below 2 eV. The Kohn calculations were the first for the (e⁺–H₂) system to treat the potential term corresponding to the H₂ molecule explicitly. This introduced a complication [1] that had been avoided in earlier applications [3–5] of the Kohn method by the use of the method of models [6].

Our implementation of the Kohn method has recently been made considerably more accurate. This is due most notably to the inclusion in the trial wavefunction of a greater number of terms describing short-range correlations between the molecular electrons and the positron, as well as to the use of improved methods for eliminating numerical anomalies due to so-called Schwartz singularities [7, 8]. We intend to publish details of our analysis of Schwartz singularities in a forthcoming article. In this paper, we will discuss results that have arisen during our efforts to improve the quality of the Kohn calculations by introducing a more flexible description of leptonic correlations than has previously been used.

Our earlier calculations [1] included in the description of the electron–positron correlation a number of terms that were linear in the electron–positron distance. The importance of such terms was first demonstrated by Hylleraas [9] and their inclusion greatly increases the speed at which the description of the electron–positron interaction converges. As explained by Armour [10], this is due to the role of linear terms in the electron–positron distance in satisfying the Kato cusp condition [11]. The use in the earlier Kohn calculations of Hylleraas-type functions in the electron–positron coordinate was seen to increase significantly both the variational estimate, ηv, of the phase shift and the estimate of Zeff, the positron annihilation parameter. The value of Zeff measures the correlation between the positron and the target molecule and can be regarded as the effective number of molecular electrons available for annihilation with the positron. Methods for determining theoretical values of Zeff in the context of our Kohn calculations have already been outlined [1].
Discrepancies remained between the results of the earlier calculations and available experimental data, and our efforts to improve the theoretical model are ongoing. We have recently extended our Kohn calculations to assess for the first time the contribution to $n_e$ and $Z_{eff}$ made by Hylleraas-type functions that are linear in the interelectronic distance. We have found that, when Hylleraas-type functions of this form are included in the description of the short-range leptonic correlations, the results of the Kohn calculations can be unreliable unless the wavefunction used to represent the target H$_2$ molecule is itself made more accurate by the inclusion of Hylleraas-type functions in the interelectronic distance. Our observations are similar to those made by Van Reeth and Humberston [12] in their Kohn calculations of s-wave phase shifts for positron scattering by atomic helium. Close-coupling calculations of s-wave phase shifts for positron scattering made by Hylleraas-type functions of this form are included in the description of the short-range leptonic correlations, and their Kohn calculations of s-wave phase shifts for positron scattering are similar to those made by Van Reeth and Humberston [12].

In our calculations on (e$^+–$H$_2$) scattering, we have found it convenient to fix the nuclei at the equilibrium internuclear separation, $R = 1.4$ au and to label the electrons as particles 1 and 2, taking the positron to be particle 3 and describing each particle by prolate spheroidal coordinates [18] $(\lambda_j, \mu_j, \phi_j)$, $j \in \{1, 2, 3\}$. We have used a complex trial wavefunction of the form

$$\Psi_i = (S + \alpha_1 \theta + p_{0} \chi_{0} + \sum_{i=1}^{M} p_{i} \chi_{i}), \quad (1)$$

where

$$T = S + iC, \quad (2)$$

and

$$S = \frac{N}{\lambda_3 - 1} \sin[c(\lambda_3 - 1)] \quad (3)$$

and

$$C = \frac{N}{\lambda_3 - 1} \cos[c(\lambda_3 - 1)][1 - \exp[-\gamma(\lambda_3 - 1)]]. \quad (4)$$

The functions $S$ and $C$ are the same as those used in our previous Kohn calculations [1] and represent, respectively, the incident and scattered positrons asymptotically far from the target H$_2$ molecule. The shielding parameter, $\gamma$, ensures that $C$ is regular at the origin and, as before [1], is taken to have the value $\gamma = 0.75$. The constant $c$ is defined to be $c = kR/2$, $k$ being the magnitude of the positron momentum in atomic units. $N$ is a normalization constant. The unknowns $a_i$ and $\{p_0, \ldots, p_M\}$ are the complex-valued constants to be determined by the Kohn variational method. The function $\psi_G$ is an approximation to the ground-state wavefunction of the unperturbed hydrogen molecule and is determined by the Rayleigh–Ritz variational method [15]. The general form of $\psi_G$ will be discussed in section 2.2.

The short-range correlation functions, $\Omega = \{\chi_0, \ldots, \chi_M\}$, allow for the description of direct electron–positron and electron–electron interactions. $\chi_0$ is the same correlation function used in our previous calculation [1] and was introduced first by Massey and Ridley [19]. The general form of the remaining functions, for $(1 \leq i \leq M)$, is

$$\chi_i = N^2 \left[ \lambda_1^{a_i} \lambda_2^{b_i} \mu_1^{c_i} \mu_2^{d_i} s_1(\theta_i) + \lambda_1^{b_i} \lambda_2^{a_i} \mu_1^{d_i} \mu_2^{c_i} s_2(\theta_i) \right] \times \lambda_3^{s_1}(\theta_i) \exp[-\beta(\lambda_1 + \lambda_2 - \lambda_3)], \quad (5)$$

for prescribed basis states, $(a_i, b_i, c_i, d_i, r_i, s_i, \theta_i)$, comprising non-negative integers. The interparticle functions, $s_{pq}(\theta_i)$, have the form

$$s_{12}(\theta_i) = \begin{cases} \rho_{12} = \frac{1}{\sqrt{M_{12}}} \cos(\phi_1 - \phi_2) \quad (\theta_i = 1) \\ M_{12} \quad (\theta_i = 2) \\ 1 \quad \text{(otherwise)} \end{cases} \quad (6)$$

and

$$s_{3j}(\theta_i) = \begin{cases} \rho_{j3} = \frac{1}{\sqrt{M_{j3}}} \cos(\phi_j - \phi_3) \quad (\theta_i = 3) \\ M_{j3} \quad (\theta_i = 4) \\ 1 \quad \text{(otherwise)} \end{cases} \quad (7)$$

2. Theory

2.1. The complex Kohn variational method

A description of the Kohn variational method is given elsewhere [2]. Calculations specific to the elastic scattering of positrons by molecular hydrogen have been carried out by Armour and coworkers [3–5] and, more recently, by Cooper and Armour [1]. Only the essential aspects of the method will be repeated here.

The objective of the calculation is to obtain an accurate approximation to the exact scattering wavefunction, $\Psi$, from which it is straightforward to calculate variational estimates, $\eta_i$, of the phase shift, as well as estimates of $Z_{eff}$. Approximate wavefunctions can be obtained by prescribing a trial wavefunction, $\Psi_i$, whose general form is known but which depends linearly on $n$ unknown parameters. The basis of the Kohn method is the application of a stationary principle that allows optimal values of these parameters to be determined by solving a corresponding system of linear equations in the $n$ unknowns.

The complex Kohn method [16] is an extension of the original variational approach and allows the trial wavefunction, $\Psi_i$, to be complex-valued. It has been shown [17] that the use of complex trial functions can mitigate the effects of anomalous results due to Schwartz singularities that arise when the linear system of Kohn equations is numerically ill-conditioned. Our own investigations of Schwartz singularities, to be discussed in a future article, have confirmed that the results presented here are free of this type of anomalous behaviour.
for \( j \in \{1, 2\} \), where \( r_{pq} \) is the distance between leptons \( p \) and \( q \). The inclusion of terms of the form \( M_{pq} \cos(\phi_p - \phi_q) \), where
\[
M_{pq} \equiv \left( \delta_+^j \lambda_j^2 - 1 \right) \left( 1 - \mu_p^j \right) \left( 1 - \mu_q^j \right)^{1/2}
\]
is equivalent to considering terms in \( r_{pq}^2 \). The choice of the nonlinear parameters, \( \alpha \) and \( \beta \), will be discussed in section 2.3.

We have carried out Kohn calculations using two different sets of correlation functions, which for convenience we shall denote by \( \Omega^{(1)} \) and \( \Omega^{(2)} \). The set \( \Omega^{(1)} \) has \( M = 279 \) and, in addition to \( \psi_0 \), contains three subsets of 87 basis functions corresponding to \( \theta_i = 0, \theta_i = 2 \) and \( \theta_i = 4 \), as well as 18 Hylleraas-type basis functions in the electron–positron coordinates, for which \( \theta_i = 3 \). \( \Omega^{(1)} \) has the same general form as the set of 99 correlation functions used in our earlier calculation [1]. The set \( \Omega^{(2)} \) has \( M = 297 \) and is identical to \( \Omega^{(1)} \) but for the inclusion of a further 18 Hylleraas-type basis functions in the interelectronic coordinate, for which \( \theta_i = 1 \). Further details of the individual basis functions used are available from the corresponding author.

2.2. The hydrogen molecule

Although the Schrödinger equation for the hydrogen molecule cannot be solved exactly, very accurate numerical approximations to the exact solution can be obtained. A standard approach for determining approximate wavefunctions of bound states is the Rayleigh–Ritz variational method, used to great effect by James and Coolidge [20] and Kołos and Roothaan [21] in their pioneering calculations on the hydrogen molecule. Following these authors, we have taken the approximate wavefunction, \( \psi_G \), to have the form
\[
\psi_G = \sum_{i=1}^{l} c_i \psi_i,
\]
where
\[
\psi_i = \frac{1}{2 \delta} \left( \lambda_1^{m_1} \lambda_2^{m_2} \mu_1^{k_1} \mu_2^{k_2} + \lambda_1^{m_1} \lambda_2^{m_2} \mu_1^{k_2} \mu_2^{k_1} \right)
\times s_{12}(\omega_0) \exp[-\delta(\lambda_1 + \lambda_2)],
\]
for prescribed basis states, \( \{m_1, n_1, j_1, k_1, \omega_0\} \), comprising non-negative integers. The function \( s_{12}(\omega_0) \) has the same definition as used in (6). Optimal values of the unknown constants \( c_i \) are determined in the Rayleigh–Ritz method by minimizing the energy expectation of \( \psi_G \).

The accuracy of \( \psi_G \) is typically measured in terms of the correlation energy of the molecule. This is the amount of the ground-state energy, due to electron correlation, beyond that which is taken into account in a Hartree–Fock calculation [15]. The percentage, \( P_C \), of the correlation energy accounted for by an approximate target wavefunction with ground-state energy expectation, \( E_{\text{calc}} \), is
\[
P_C = \frac{E_{\text{calc}} - E_{\text{HF}}}{E_{\text{ex}} - E_{\text{HF}}} \times 100,
\]
where \( E_{\text{ex}} \) is the exact nonrelativistic ground-state energy in the Born–Oppenheimer approximation [22] and \( E_{\text{HF}} \) is the Hartree–Fock energy.

We have carried out Kohn calculations using two different target wavefunctions, which for convenience we shall denote by \( \psi^{(A)}_G \) and \( \psi^{(B)}_G \). The function \( \psi^{(A)}_G \) has \( L = 144 \), with a basis set comprising 72 terms having \( \omega_0 = 0 \) and 72 terms having \( \omega_0 = 2 \). A value of \( \delta = 1.14 \) was chosen for \( \psi^{(A)}_G \) to minimize its ground-state energy expectation value, which accounted for 96.8% of the correlation energy of \( \text{H}_2 \). \( \psi^{(A)}_G \) has the same general form as the 31-term function used in our earlier calculations [1]. The function \( \psi^{(B)}_G \) has a 145-term basis set of an identical form to that used for \( \psi^{(A)}_G \), but for the inclusion of one Hylleraas-type term in \( \rho_{12} \) for which \( \omega_0 = 1 \). The value of \( \delta \) for \( \psi^{(B)}_G \) remained fixed at \( \delta = 1.14 \), and the corresponding ground-state energy accounted for 99.7% of the correlation energy of \( \text{H}_2 \). Further details of the individual basis functions used are available from the corresponding author. The values of \( E_{\text{HF}} \) and \( E_{\text{ex}} \) used to determine \( P_C \) were taken respectively from the calculations of Jensen [23] and Wolniewicz [24].

The important role played by Hylleraas-type functions in \( \rho_{12} \) in describing electronic correlations in the hydrogen molecule has long been known [20]. However, until very recently it was not feasible for us to carry out Kohn calculations with target functions of this form, due to difficulties in evaluating the corresponding integrals found in the Kohn equations. However, we have successfully made modifications to the computational framework used in our calculations so that target functions containing Hylleraas-type terms in \( \rho_{12} \) can now be admitted. Earlier changes to this framework had already been made during our previous calculations [1], where code designed originally for investigations of helium–antihydrogen scattering [25] was adapted so that it could be applied to \((e^+–\text{H}_2)\) scattering. Those initial modifications allowed for the evaluation of integrals containing terms in \( \rho_{13}\rho_{23}/\rho_{12} \) by using a triple Neumann expansion [26, 27]. To carry out the calculations described here involving \( \psi^{(B)}_G \), it was necessary to extend these modifications to allow for the evaluation of integrals containing factors of the form
\[
G_{123} = F(\lambda_3) \frac{\rho_{12}\rho_{23}}{\rho_{13}},
\]
and
\[
G_{213} = F(\lambda_2) \frac{\rho_{12}\rho_{13}}{\rho_{23}},
\]
where \( F(\lambda) \) can be either of the two open-channel functions (3), (4) representing the positron, or the function \( \chi_0 \).

2.3. Optimization

In contrast to variational calculations of bound states, there is no energy minimization principle associated with scattering wavefunctions. As a result, there is no absolutely rigorous method available to optimize the nonlinear parameters, \( \alpha \) and \( \beta \), characterizing the rate of decay of the short-range correlation functions. Nevertheless, arguments for preferred choices of these parameters can be made.

For atomic scattering, it has been shown [28] that, for a system where no bound state exists, the Kohn method gives an upper bound on the scattering length, \( a \), where
\[
a = \lim_{k \to 0} \left( -\frac{\tan \eta}{k} \right),
\]
and hence a lower bound on the exact phase shift, $\eta_k$, in the limit of zero positron energy. In the case of the Kohn variational method, obtaining bounds on scattering phase shifts is not generally possible at all incident energies considered, owing to the occurrence of the Schwartz anomalous behaviour at certain energies. However, an analysis of the method for potential scattering by Brownstein and McKinley [29] showed that, away from these energies, the phase shift will be bounded, provided the trial functions are, in some sense, sufficiently accurate.

In the case of the solution of scattering systems using a close-coupling expansion [30], it has been shown that bounds exist on scattering phase shifts or eigenphase sums provided that all open channels are included in the expansion and that the open channel target states are exact [31, 32]. If additional correlation functions are added to the expansion over target states, the bounds are still valid under certain conditions [31, 32], the extra terms acting as an optical potential for channels not explicitly included.

Kohn calculations using exact target states have been carried out by Humberston and are described, for example, in [26]. He found that, at low energies, the variational approximation to the phase shift tended to increase monotonically as the flexibility of the trial wavefunction was improved by the inclusion of a greater number of short-range correlation functions. He concluded that it was reasonable to expect the variational approximation to converge upwards to the exact phase shift with the use of an increasingly flexible trial wavefunction. In the method of models it is assumed that the target wavefunction used in the calculation is an exact trial wavefunction. In the method of models it is assumed that all open channels are included in the expansion and that the exact phase shift with the use of an increasingly flexible correlation functions, $\psi^{(A)}_G$ and $\psi^{(B)}_G$. In a self-evident nomenclature, we will denote the four different trial wavefunctions by $\psi^{(1,A)}_1$, $\psi^{(2,A)}_1$, $\psi^{(1,B)}_1$ and $\psi^{(2,B)}_1$. Values of $\eta_k$ and $Z_{eff}$ were determined for each trial wavefunction, for positron momenta in the range $k = 0.01$ au. to $k = 0.4$ au, corresponding to a maximum positron energy of 2.18 eV. As noted in section 1, higher partial waves become significant in scattering processes above this energy.

Following our discussion in section 2.3, we selected values of $\alpha$ and $\beta$ approximately to maximize $\eta_k$. In principle, such maxima could be found, at least numerically, by straightforward iterative approaches. In practice, however, repeating our Kohn calculations for different values of $\alpha$ and $\beta$ is computationally very expensive; as we have discussed elsewhere [1], each iteration necessitates the evaluation of a large number of integrals that can be obtained only numerically via a triple Neumann expansion. Our analyses were therefore restricted to a relatively small set of candidate values for the nonlinear parameters, namely, $\alpha \in \{0.2, 0.3, \ldots, 0.9, 1.0\}$ and $\beta \in \{0.2, 0.3, \ldots, 1.4, 1.5\}$. Kohn calculations were performed for each of the 126 combinations of $\alpha$ and $\beta$. Unless otherwise noted, all of the results presented here are from calculations carried out with $\alpha = 0.3$ and $\beta = 0.7$, which we found to maximize $\eta_k$ for the trial wavefunction, $\psi^{(1,A)}_1$, at $k = 0.04$. This value of $k$ is approximately equal to the average momentum of a Maxwellian distribution of positrons at 297 K. It is convenient to consider the positron distribution at this temperature as it allows a direct comparison to be made of our results for $Z_{eff}$ with experimental data.

3. Results and discussion

Our calculations were carried out for the lowest partial wave of $\Sigma^\pi_1$ symmetry. A total of four different trial wavefunctions were used, corresponding to combinations of the two sets of correlation functions, $\Omega_1^{(1)}$ and $\Omega_1^{(2)}$, and the two inexact target functions, $\psi^{(A)}_G$ and $\psi^{(B)}_G$. In a self-evident nomenclature, we will denote the four different trial wavefunctions by $\psi^{(1,A)}_1$, $\psi^{(2,A)}_1$, $\psi^{(1,B)}_1$ and $\psi^{(2,B)}_1$. Values of $\eta_k$ and $Z_{eff}$ were determined for each trial wavefunction, for positron momenta in the range $k = 0.01$ au. to $k = 0.4$ au, corresponding to a maximum positron energy of 2.18 eV. As noted in section 1, higher partial waves become significant in scattering processes above this energy.

Figure 1. $\eta_k(k)$ for $[\times]\psi_1^{(1,A)}$, $[+]*\psi_1^{(2,A)}$ and $[O]$ reported by Armour and Baker [4].

3.1. Calculations involving $\psi^{(A)}_G$

We consider first the two trial wavefunctions involving $\psi^{(A)}_G$, having $P_{c} = 96.8$. The dependence of $\eta_k$ and $Z_{eff}$ on $k$ for $\psi^{(1,A)}_1$ and $\psi^{(2,A)}_1$ is shown in figures 1 and 2. We have also included in these figures the values of $\eta_k$ and $Z_{eff}$ found in table 2(e) of the account of Kohn calculations made by Armour and Baker [4]. Those calculations used the method of models with a trial wavefunction containing $M = 72$ correlation functions, including eight Hylleraas-type terms in the electron–positron distance.
The effect of including in $\Psi_i^{(2,A)}$ the Hylleraas-type correlation functions in $\rho_{12}$ is clear. The calculated values of both $\eta_v$ and $Z_{\text{eff}}$ for $\Psi_i^{(2,A)}$ are significantly greater at low positron momenta than the corresponding values for $\Psi_i^{(1,A)}$. The differences between the results for $\Psi_i^{(1,A)}$ and $\Psi_i^{(2,A)}$ become smaller at higher positron momenta. There is broad agreement between our results for $\eta_v$ and those reported by Armour and Baker, although there are insufficient data available from those calculations to determine whether better agreement is observed for $\Psi_i^{(1,A)}$ or $\Psi_i^{(2,A)}$. Estimates, $\sigma_v$, of the total scattering cross section could also be determined directly from values of $\eta_v$. However, there is a paucity of available experimental cross-section data at the very low positron momenta of most interest here, making any meaningful comparison with our results very difficult.

There is good agreement between the estimates of $Z_{\text{eff}}$ for $\Psi_i^{(1,A)}$, $\Psi_i^{(2,A)}$ and the results of Armour and Baker, for $k \geq 0.1$. Again, a lack of available data from those earlier calculations prevents a comparison below $k = 0.1$, where the differences between the results for $\Psi_i^{(1,A)}$ and $\Psi_i^{(2,A)}$ are striking. We can, however, remark that the calculated value of $Z_{\text{eff}}$ for $\Psi_i^{(2,A)}$ at $k = 0.04$ is 13.4, in reasonable agreement with the accepted experimental value of $Z_{\text{eff}} = 14.61 \pm 0.14$ at 297 K [33].

The extent of the influence on $\eta_v$ and $Z_{\text{eff}}$ of the Hylleraas-type functions in $\rho_{12}$ becomes even more pronounced if the values of the nonlinear parameters, $\alpha$ and $\beta$, are varied. Figures 3 and 4 illustrate the respective dependence of $\eta_v$ and $Z_{\text{eff}}$ on $\alpha$ and $\beta$ at $k = 0.04$, for $\Psi_i^{(1,A)}$ and $\Psi_i^{(2,A)}$. The effects of the Hylleraas-type functions in $\rho_{12}$ included in $\Psi_i^{(2,A)}$ are most obvious for $\alpha < 0.5$ and become more dramatic as the value of $\alpha$ decreases. Indeed, the values of $\eta_v$ and $Z_{\text{eff}}$ for $\Psi_i^{(2,A)}$ shown in figures 3 and 4 have not reached an obvious plateau with respect to further decreases in the value of $\alpha$. It seems plausible that these values would continue to increase with decreasing $\alpha$.

In view of this, we think it necessary to examine the possibility that the observed effect is not genuine and instead arises from inaccuracies in the numerical evaluation of the integrals required to formulate the Kohn equations. These could occur because the short-range correlation functions become more diffuse as the value of $\alpha$ decreases, increasing the range of the configuration space of the positron over which the effects of the correlation functions are significant.
To investigate this, we carried out a more detailed study of the Kohn calculations at $(\alpha, \beta) = (0.2, 1.1)$ and $(\alpha, \beta) = (0.2, 0.8)$, corresponding respectively to the maximum values of $\eta_v$ and $Z_{\text{eff}}$ observed for $\Psi_1^{(A)}$ in figures 3 and 4. If the effects observed for $\Psi_1^{(A)}$ are due to problems with convergence of integrals, increasing the range of integration in $\lambda$ should have a significant effect on the results for $\eta_v$ and $Z_{\text{eff}}$. However, when we increased the range of our integration in $\lambda$ by 50%, the values of $\eta_v$ at $(\alpha, \beta) = (0.2, 1.1)$ and $Z_{\text{eff}}$ at $(\alpha, \beta) = (0.2, 0.8)$ changed respectively by only 0.1% and 0.2% from the values shown for $\Psi_1^{(A)}$ in figures 3 and 4. This is clear evidence that the effects we have described are not due to errors in the numerical integration.

Figures 1–4 indicate that the apparent importance of the Hylleraas-type correlation functions in $\rho_{12}$ is a general feature of the calculation at low positron momenta. This is unexpected, since functions of this type do not address explicitly the key difficulty of describing correlations in terms of the electron–positron separation. Following our discussion in section 2.3, it is conceivable that the observed behaviour is a result of inaccuracies in the calculation due to the use of the inexact target wavefunction, $\psi_G^{(A)}$, despite its taking into account of 96.8% of the correlation energy. This claim is consistent with the findings of Van Reeth and Humberston [12]. In light of their conclusions, we investigated the sensitivity of our own Kohn calculations to changes in the accuracy of the target wavefunction. Basis functions were removed incrementally from $\psi_G^{(A)}$, creating a series of target wavefunctions of successively lower accuracies. After each removal, Kohn calculations were performed using the target wavefunction of reduced accuracy to determine values of $\eta_v$ and $Z_{\text{eff}}$, each time for two trial wavefunctions having the sets of correlation functions $\Omega^{(1)}$ and $\Omega^{(2)}$. A maximum of 70 basis functions were removed from the original set of 144 terms, at which point the target wavefunction accounted for 90.7% of the correlation energy of $H_2$. The dependence of $\eta_v$ and $Z_{\text{eff}}$ on the accuracy, $P_c$, of each target wavefunction is shown in figures 5 and 6, respectively, for $k = 0.04$.

The values of $\eta_v$ and $Z_{\text{eff}}$ tend to decrease with increasing $P_c$, for both $\Omega^{(1)}$ and $\Omega^{(2)}$. However, there is a distinct convergence of $\eta_v$ and $Z_{\text{eff}}$ for the results corresponding to $\Omega^{(1)}$ above $P_c \sim 96$, which is not evident for the results corresponding to $\Omega^{(2)}$. More generally, we have observed similar behaviour for analogous calculations performed at different values of $k$. We can reasonably conclude that Kohn calculations carried out using $\psi_G^{(A)}$ are reliable when Hylleraas-type terms in $\rho_{12}$ are omitted from the correlation functions, but are unreliable when functions of this type are included. For trial wavefunctions containing the set of correlation functions, $\Omega^{(2)}$, we would expect any further increase in the accuracy of the target wavefunction to be accompanied by a noticeable drop in the values of $\eta_v$ and $Z_{\text{eff}}$.

3.2. Calculations involving $\psi_G^{(B)}$

We consider now the two trial wavefunctions involving $\psi_G^{(B)}$, having $P_c = 99.7$. The corresponding Kohn calculations could be performed only when the modifications to the computational framework, described in section 2.2, had been implemented. The dependence of $\eta_v$ and $Z_{\text{eff}}$ on $k$ for $\Psi_1^{(1,B)}$ and $\Psi_1^{(2,B)}$ is shown in figures 7 and 8. We have also reproduced in these figures the values of $\eta_v$ and $Z_{\text{eff}}$ determined earlier for $\Psi_1^{(1,A)}$ and $\Psi_1^{(2,A)}$.

A number of comments should be made about our results. Firstly, there is excellent agreement in the values of $\eta_v$ and $Z_{\text{eff}}$ between calculations using $\Psi_1^{(1,A)}$ and $\Psi_1^{(1,B)}$, substantiating...
our earlier claim that $\psi_{G}^{(A)}$ is a sufficiently accurate target wavefunction for the Kohn calculation using $\Psi_{t}^{(1,A)}$ to have converged and hence to be considered reliable. Secondly, there are significant differences in the results for $\Psi_{t}^{(2,A)}$ and $\psi_{G}^{(B)}$. The improvement in the accuracy of the target wavefunction has brought the results for $\psi_{G}^{(B)}$ broadly into line with those for $\Psi_{t}^{(1,A)}$ and $\Psi_{t}^{(1,B)}$. When the more accurate Kohn calculations using $\psi_{G}^{(B)}$ are carried out, therefore, the effect of including Hylleraas-type correlation functions in $\rho_{12}$ is small.

It remains to be shown that $\psi_{G}^{(B)}$ is a sufficiently accurate target wavefunction for calculations involving $\Psi_{t}^{(2,B)}$ to be considered reliable. To do this, we again removed basis functions successively at random from the target wavefunction to reduce its accuracy. After each removal, Kohn calculations were performed using the target wavefunction of reduced accuracy to determine values of $\eta_{v}$ and $Z_{\text{eff}}$, each time for two trial wavefunctions having the sets of correlation functions $\Omega^{(1)}$ and $\Omega^{(2)}$. A maximum of 104 basis functions were removed from the original set of 145 terms comprising $\psi_{G}^{(B)}$, at which point the target wavefunction accounted for 90.4% of the correlation energy of $H_{2}$. The first 70 terms removed corresponded directly to the 70 terms removed earlier from $\psi_{G}^{(A)}$. Thereafter, the remaining 34 terms were removed successively at random, with the condition that the Hylleraas-type term in $\rho_{12}$ was not removed. The dependence of $\eta_{v}$ and $Z_{\text{eff}}$ on the accuracy, $P_{C}$, of each target wavefunction is shown in figures 9 and 10 respectively, for $k = 0.04$.

The convergence of $\eta_{v}$ and $Z_{\text{eff}}$ with increasing $P_{C}$ is not as obvious as it was in the previous calculations illustrated in figures 5 and 6; however, the slopes of the curves in figures 9 and 10 are becoming noticeably flat in the upper limit of $P_{C}$. We have already concluded that the Kohn calculations involving $\Psi_{t}^{(1,A)}$, and hence those involving $\Psi_{t}^{(1,B)}$, are reliable. Further, the behaviour of the curves corresponding to $\Omega^{(1)}$ and $\Omega^{(2)}$ is very similar in the limit of high $P_{C}$ in both figures 9 and 10. Inspection of these figures suggests that neither set of results would change significantly if the target wavefunction was again extended to account for most of the remaining 0.3% of the correlation energy. We may reasonably regard the calculations involving $\Psi_{t}^{(2,B)}$ as reliable.

An interesting feature apparent from figures 9 and 10 is that the inclusion of the Hylleraas-type term in $\rho_{12}$ raises the threshold of convergence for trial wavefunctions containing $\Omega^{(1)}$. In these figures, the values of $\eta_{v}$ and $Z_{\text{eff}}$ are still clearly declining at $P_{C} = 96$, at which value we have already concluded that Kohn calculations containing $\Omega^{(1)}$, using target wavefunctions without Hylleraas-type terms, have converged. The origin of this effect is not clear and will remain a subject of our investigations.

4. Concluding remarks

We have demonstrated that the reliability of Kohn calculations for $e^{+}$–$H_{2}$ scattering can depend upon the flexibility of the correlation functions used in the trial wavefunction, relative to the flexibility and the accuracy of the approximate wavefunction representing the target. This dependence is most prominent at very low positron momenta. Our findings are similar to those reported by Van Reeth and Humberston for positron–helium scattering and highlight the need for rigorous testing of the accuracy of Kohn calculations whenever inexact target wavefunctions are used.

We have implemented a numerical method to test the stability of any given calculation to variations in the accuracy of the approximate target state. This has allowed us to distinguish between reliable and unreliable results and thus compensate for the lack of explicit bounds on the scattering phase shifts.
Having carried out the most accurate of our Kohn calculations, we have observed that the effect of including Hylleraas-type correlation functions in \( \rho_{12} \) is to increase the calculated values of \( \eta \) only slightly. The changes in the values of \( Z_{\text{eff}} \) are also small, so that there is still disagreement between our reported values and the established experimental result of \( Z_{\text{eff}} = 14.61 \pm 0.14 \) at 297 K [33]. This discrepancy is significant when compared to the results of other applications of the Kohn method for simpler systems. The best available calculations for atomic helium [34], for example, obtain a theoretical value of \( Z_{\text{eff}} = 3.88 \pm 0.01 \) at 293 K. The experimental value is 3.94 \pm 0.02 [35]. Our intention is to address the problems in our Kohn calculations for \( \text{H}_2 \) by improving the flexibility of the correlation functions still further to include, for example, terms linear in both \( \rho_{12} \) and \( \rho_{13} \), \( j \in \{1, 2\} \), as well as terms describing virtual positronium formation. Consideration of virtual positronium has been shown [36] to enhance significantly the calculated values of \( Z_{\text{eff}} \) for positron scattering by atomic hydrogen near the positronium formation threshold. We hope that a similar increase in \( Z_{\text{eff}} \) will be observed in our own calculations for molecular hydrogen if virtual positronium formation is taken into account. In any event, we will try to obtain converged results with as flexible a set of short-range correlation functions as possible.

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References

[1] Cooper J N and Armour E A G 2008 Nucl. Instrum. Methods B 266 452–7
[2] Kohn W 1948 Phys. Rev. 74 1763–72
[3] Armour E A G, Baker D J and Plummer M 1990 J. Phys. B: At. Mol. Phys. 23 3087–74
[4] Armour E A G and Baker D J 1987 J. Phys. B: At. Mol. Phys. 20 6105–19
[5] Armour E A G 1988 Phys. Rep. 169 1–98
[6] Drachman R J 1972 J. Phys. B: At. Mol. Phys. 5 L30–2
[7] Schwartz C 1961 Phys. Rev. 124 1468–71
[8] Nestet R K 1968 Phys. Rev. 175 134–42
[9] Hylleraas E A 1929 Z. Phys. 54 347–66
[10] Armour E A G 1985 J. Phys. B: At. Mol. Phys. 18 3361–8
[11] Kato T 1957 Commun. Pure Appl. Math. 10 151–7
[12] Van Reeth P and Humberston J W 1995 J. Phys. B: At. Mol. Opt. Phys. 28 L23–8
[13] Plummer M, Noble C J and De Loustau M 2004 J. Phys. B: At. Mol. Opt. Phys. 37 2979–96
[14] Zatsarinny O, Bartschat K and Taya S S 2006 J. Phys. B: At. Mol. Opt. Phys. 39 1237–49
[15] Bransden B H and Joachain C J 2003 Physics of Atoms and Molecules (Harlow: Prentice Hall)
[16] McCurdy C W, Rescigno T N and Schneider B I 1987 Phys. Rev. A 36 2061–6
[17] Schneider B I and Rescigno T N 1988 Phys. Rev. A 37 3749–54
[18] Flammer C 1957 Spherical Wave Functions (Stanford, CA: Stanford University Press)
[19] Massey H S W and Ridley R O 1956 Proc. Phys. Soc. A 69 659–67
[20] James H M and Coolidge A S 1933 J. Chem. Phys. 1 285–35
[21] Kolos W and Roothaan C C J 1960 Rev. Mod. Phys. 32 219–32
[22] Born M and Oppenheimer R 1927 Ann. Phys., Lpz. 84 457–84
[23] Jensen F 1999 J. Chem. Phys. 110 6601–5
[24] Wolniewicz L 1995 J. Chem. Phys. 103 1792–9
[25] Armour E A G, Todd A C, Jonsell S, Liu Y, Gregory M R and Plummer M 2008 Nucl. Instrum. Methods B 266 363–8
[26] Armour E A G and Humberston J W 1991 Phys. Rep. 204 165–251
[27] Plummer M, Armour E A G, Todd A C and Cooper J N 2007 Frontiers 2007, Computational Science and Engineering Department, Daresbury and Rutherford Laboratories Annual Report (Science and Technology Facilities Council, UK) pp 6–7
[28] Spruch L and Rosenberg L 1959 Phys. Rev. 116 1034–40
[29] Brownstein K R and McKinley W A 1968 Phys. Rev. 170 1255–66
[30] Bransden B H 1983 Atomic Collision Theory (Reading, MA: Benjamin/Cummings) p 223
[31] Hahn Y, O’Malley T F and Spruch L 1964 Phys. Rev. 134 B 397–404
[32] Hahn Y, O’Malley T F and Spruch L 1964 Phys. Rev. 134 B 911–9
[33] Gaulitis M 1965 Sov. Phys.–JETP 20 107–17
[34] Laricchia G, Carlton M, Beling C D and Griffith T C 1987 J. Phys. B: At. Mol. Phys. 20 1865–74
[35] Van Reeth P, Humberston J W, Iwata K, Greaves R G and Surko C M 1996 J. Phys. B: At. Mol. Opt. Phys. 29 L465–71
[36] Coleman P G, Griffith T C, Heyland G R and Killeen T L 1975 J. Phys. B: At. Mol. Phys. 8 1734–43
[37] Van Reeth P and Humberston J W 1998 J. Phys. B: At. Mol. Opt. Phys. 31 L231–8