

## The stability of S-states of unit-charge Coulomb three-body systems: from H- to H2+

Andrew W King, Frank Longford, Hazel Cox

### Publication date

01-01-2013

### Licence

This work is made available under the [CC BY 4.0](#) licence and should only be used in accordance with that licence. For more information on the specific terms, consult the repository record for this item.

### Document Version

Published version

### Citation for this work (American Psychological Association 7th edition)

King, A. W., Longford, F., & Cox, H. (2013). *The stability of S-states of unit-charge Coulomb three-body systems: from H- to H2+* (Version 1). University of Sussex. <https://hdl.handle.net/10779/uos.23416184.v1>

### Published in

Journal of Chemical Physics

### Link to external publisher version

<https://doi.org/10.1063/1.4834036>

### Copyright and reuse:

This work was downloaded from Sussex Research Open (SRO). This document is made available in line with publisher policy and may differ from the published version. Please cite the published version where possible. Copyright and all moral rights to the version of the paper presented here belong to the individual author(s) and/or other copyright owners unless otherwise stated. For more information on this work, SRO or to report an issue, you can contact the repository administrators at [sro@sussex.ac.uk](mailto:sro@sussex.ac.uk). Discover more of the University's research at <https://sussex.figshare.com/>

**The stability of S-states of unit-charge Coulomb three-body systems: From H to H<sub>2</sub> +**

Andrew W. King, Frank Longford, and Hazel Cox

Citation: *The Journal of Chemical Physics* **139**, 224306 (2013); doi: 10.1063/1.4834036

View online: <http://dx.doi.org/10.1063/1.4834036>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/139/22?ver=pdfcov>

Published by the [AIP Publishing](#)

---



## Re-register for Table of Content Alerts

Create a profile.



Sign up today!



# The stability of S-states of unit-charge Coulomb three-body systems: From $H^-$ to $H_2^+$

Andrew W. King, Frank Longford, and Hazel Cox<sup>a)</sup>

Department of Chemistry, University of Sussex, Falmer, Brighton BN1 9QJ, United Kingdom

(Received 5 September 2013; accepted 12 November 2013; published online 11 December 2013)

High accuracy non-relativistic quantum chemical calculations of the ground state energies and wavefunctions of symmetric three-particle Coulomb systems of the form  $\{m_1^\pm m_2^\pm m_3^\mp\}$ ,  $m_1 = m_2$ , are calculated using an efficient and effective series solution method in a triple orthogonal Laguerre basis set. These energies are used to determine an accurate lower bound to the stability zone of unit-charge three-particle Coulomb systems using an expression for the width of the stability band in terms of  $g$ , the fractional additional binding due to a third particle. The results are presented in the form of a reciprocal mass fraction ternary diagram and the energies used to derive a parameterised function  $g(a_3)$ , where  $a_3 = m_3^{-1}/(m_1^{-1} + m_2^{-1} + m_3^{-1})$  is the reciprocal mass of the uniquely charged particle. It is found that the function is not minimal at  $a_3 = 0$  which corresponds to  $\infty H^-$  nor is it minimal at the positronium negative ion ( $Ps^-$ ) the system with the least absolute energetic gain by association with a third particle; the function  $g(a_3)$  is minimal at  $m_1/m_3 = 0.49$ , and a possible physical interpretation in terms of the transition from atomic-like to molecular-like is provided. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4834036>]

## I. INTRODUCTION

Quantum chemistry is dominated by methods based on two major approximations: the Born-Oppenheimer (B-O) approximation and the orbital approximation (within Kohn-Sham theory or wavefunction-based theory). While for most applications such methods are perfectly adequate, being able to provide both qualitative and quantitative insight into the structure, bonding, reactivity, and spectroscopy of systems of experimental interest<sup>1</sup> and often to the level of “chemical accuracy,” there are systems for which these “standard” quantum chemical techniques are unsatisfactory. Thus, for example, the B-O approximation fails to correctly account for the occurrence of conical intersections. Furthermore, there is a need to ensure methods remain competitive with the increasingly accurate experimental work, for example, on molecular spectra.<sup>2</sup> There are several examples in the recent literature that advance these approximations, to name just a few, see the work by Cederbaum,<sup>3</sup> Sutcliffe,<sup>4</sup> regarding going beyond the standard B-O approximation and the work by Gill *et al.*<sup>5</sup> attempting to provide a “universally accurate and efficient approach” to electron correlation.

Here, we present the results of high accuracy, non-relativistic, quantum chemical calculations of the energy levels and wavefunctions of three-particle systems. Such systems hold a unique position, as they represent the simplest problem that encompasses both atomic and molecular ions. Usually an assumption about the structure of a particular system – atomic or molecular – is made *a priori* and then the Schrödinger equation solved accordingly; however, when the masses of the particles are similar the justification for the clamped nucleus or the Born-Oppenheimer approximation is not appropriate,

and as highlighted by Mátyus *et al.*<sup>6</sup> this qualitatively different description of “atomic” and “molecular” systems does not follow from a purely mathematical discussion. In this paper, we unify the treatment of atomic and molecular systems of the form  $\{m_1^\pm m_2^\pm m_3^\mp\}$  by treating all particle masses as finite and using a Laguerre-based wavefunction with two nonlinear parameters. This allows us to move smoothly from atomic-like to molecular-like systems. The results also provide highly accurate data for electron-correlated atomic systems (such as  $H^-$ ) and non-B-O molecular systems (such as  $H_2^+$ ). The former is relevant, for example, for those involved in density function theory developments.<sup>7</sup>

An additional reason for the importance of three-particle systems is that there are many three-particle Coulomb systems, including those involving elementary particles, such as positrons, muons, protons, and their anti-matter counterparts, that are of topical interest to both the chemistry and physics communities. For example,  $d^{+t^+}\mu^-$  is known to catalyse nuclear fusion at room temperature<sup>8–10</sup> and the recent discrepancy between determinations of the proton radius using muonic hydrogen spectroscopy involved consideration of weakly bound three-body systems such as  $(p\mu e)^-$  and  $(pp\mu)^+$ .<sup>11</sup> Furthermore, the muonium negative ion ( $e^-e^-\mu^+$ ) has been observed as an impurity during muon spin resonance spectroscopy used to probe hydrogen impurities in semiconductors and a range of materials.<sup>12</sup> Particularly relevant to such studies is an understanding of the stability of three-body Coulomb system, i.e., the conditions under which a bound state is formed. This matter is specifically addressed in the present work.

Several investigators have attempted to predict the stability of Coulombic three-particle systems based on their mass ratios.<sup>11,13–21</sup> Whereas some have attempted to use mass ratios to predict the stability of specific exotic systems such as

<sup>a)</sup>Electronic mail: h.cox@sussex.ac.uk

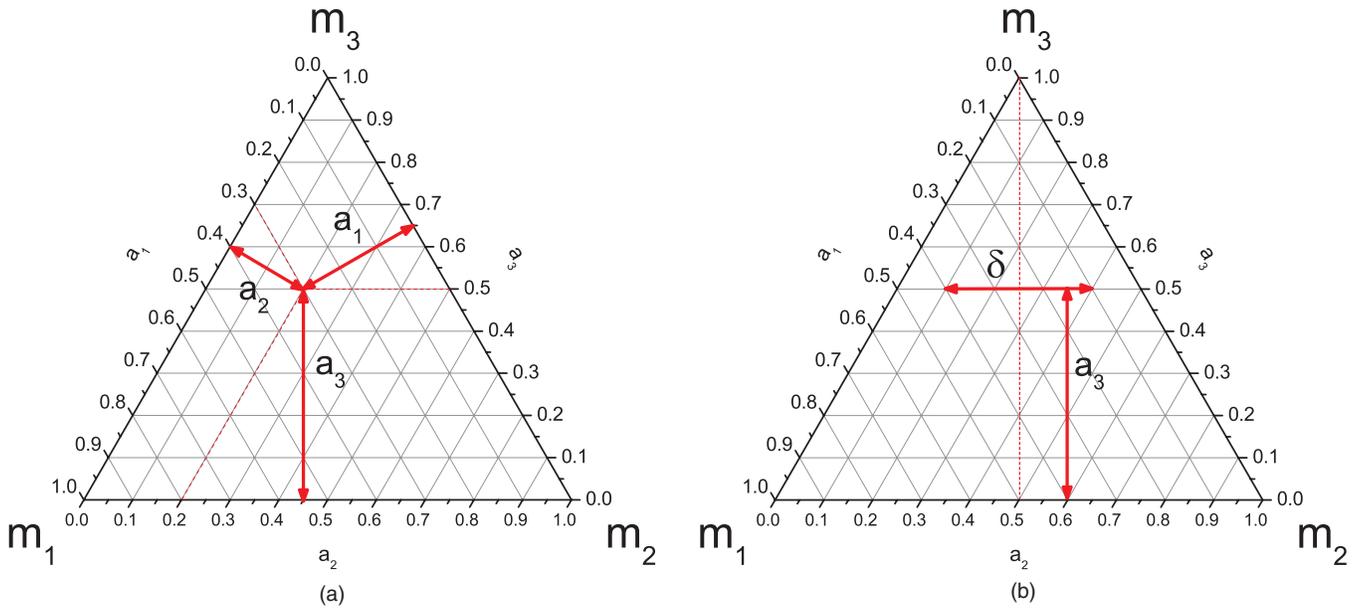


FIG. 1. (a) Reciprocal mass fractions as coordinates on a ternary diagram and (b) the width of the stability band  $\delta(a_3)$  about the  $m_1 = m_2$  symmetry axis (dashed line) for a given value of  $a_3$ .

$p^+e^+e^-$ ,<sup>14,15</sup> and  $p^+\mu^-e^-$ ,<sup>11,20</sup> others have focussed on developing a general understanding of the role that mass ratios play in the binding energy of Coulombic three-particle systems.<sup>13,16–18,21</sup> Stability of a system in this work is defined as the existence of at least one bound state below the lowest continuum threshold.<sup>22</sup>

Here, we consider three-body systems of the form  $\{m_1^\pm m_2^\pm m_3^\mp\}$  interacting via a Coulomb potential but without recourse to the clamped-nucleus or Born-Oppenheimer approximation. In the case of three-body atoms or ions, there is a unique choice of a body-fixed coordinate system for states with angular momentum  $J = 0$ , namely, that in which the three particles define a plane and the translation-free internal coordinates are chosen to be the inter-particle distances.<sup>23</sup> It is a property of Coulomb interaction that all masses can be scaled, and given that the inverse masses occur linearly in the Hamiltonian, Martin *et al.*<sup>13</sup> have shown that all possible cases can be plotted on a ternary diagram, as shown in Figure 1(a), in terms of the normalised reciprocal mass fraction coordinates,

$$a_i = \frac{1/m_i}{1/m_1 + 1/m_2 + 1/m_3}, \quad i = 1, 2, \text{ or } 3 \quad (1)$$

such that

$$a_1 + a_2 + a_3 = 1. \quad (2)$$

Hill<sup>24</sup> proved that all symmetric ( $m_1 = m_2$ ) systems are stable against dissociation into a two-particle system and a free particle, but no such formal proof exists for atoms and molecules of the general form  $\{m_1^\pm m_2^\pm m_3^\mp\}$ , where  $m_1 \neq m_2$  and, in fact, such systems are only stable within a certain range of particle mass.<sup>19</sup> Martin *et al.*<sup>13</sup> estimated the lower bound of this stability region by deriving a function,  $\delta(a_3)$ , defined in Eq. (3), for the horizontal width of the stability band, Figure 1(b), in terms of  $g(a_3)$ , where  $g$  is the fraction of additional binding gained by association with a third particle in symmetric systems and  $a_3$  is the reciprocal mass of the

uniquely charged particle

$$\delta(a_3) \geq \frac{2}{\sqrt{3}} \frac{g(a_3)}{1 + g(a_3)} (1 + a_3). \quad (3)$$

The purpose of this paper is twofold. First, we describe an improvement in the rate of energy convergence compared to previous calculations by Cox *et al.*,<sup>23,25</sup> on inclusion of additional nonlinear parameters in the wavefunction. The optimum wavefunction is used to calculate accurate energies,  $E_0$ , for a wide range of unit-charge, symmetric, three-body systems of the form  $\{m_1^\pm m_2^\pm m_3^\mp\}$ , involving the particles listed in Table I. There are 36 distinct, symmetric, singly charged ions ranging from atomic to molecular (72 including the anti-particle counterparts which, by charge inversion invariance, have the same energy as those presented, e.g.,  $E(p^+p^+e^-) = E(p^-p^-e^+)$ ). Additionally, some hypothetical mass systems are calculated to ensure an even distribution of data points along the symmetric axis of the reciprocal mass fraction

TABLE I. Masses of the particles (and anti-particles) used in this work.<sup>32</sup> These are to be compared with the values (in units of  $m_e$ ) used in previous calculations:  $m_\mu = 206.768\,262$ , Refs. 30, 33, 39, and 40,  $m_\mu = 206.768\,275$ , Ref. 41,  $m_p = 1836.152\,701$ , Refs. 30, 33, and 42,  $m_p = 1836.152\,667\,5$ , Ref. 39,  $m_d = 3670.483\,014$ , Refs. 30, 33, and 43, and  $m_t = 5495.688\,449$ , Ref. 41. Note, the masses of Frolov<sup>41</sup> have been converted from  $\text{MeV}/c^2$  using the conversion  $m_e = 0.510\,998\,928\, \text{MeV}$ <sup>32</sup> and use the most recent experimental values; his  $m_p$  and  $m_d$  values are in complete agreement with those used in the present work.

Particle	Symbol	Mass ( $m_{\text{particle}}/m_e$ )
Electron	$e^-$	1
Muon	$\mu^-$	206.768 284 3
Tauon	$\tau^-$	3477.15
Proton	$p^+/H^+$	1836.152 672 45
Deuteron	$d^+/D^+$	3670.482 965 2
Triton	$t^+/T^+$	5496.921 526 7

ternary diagram. Second, accurate values of the fractional additional binding  $g$  are calculated using these  $E_0$  values. The expression of Martin *et al.*<sup>13</sup> for the width of the stability band (3) is used to determine an accurate lower bound to the stability zone of three-particle Coulomb systems, and the results are presented on a ternary diagram.<sup>13,22</sup> Additionally, we present a functional fit of  $g(a_3)$ . It is found that the mass ratio corresponding to the minimum in the function  $g$  falls neatly in the range predicted by Mátyus *et al.*<sup>6</sup> as the point at which molecular structure emerges in three-particle systems.

## II. METHOD

The non-relativistic Schrödinger equation for the S-states of  $\{m_1^\pm m_2^\pm m_3^\mp\}$  three-body systems is solved using the method described by Cox *et al.*<sup>23</sup> In brief, the centre of mass motion is separated off and the internal coordinates are chosen as the inter-particle distances  $r_1$ ,  $r_2$ , and  $r_3$  which are, respectively, the 3-1, 3-2, and 1-2 inter-particle coordinates. The problem is then recast in perimetric coordinates<sup>26</sup> defined as  $z_i = r_j + r_k - r_i$ , where  $i, j, k$  denote cyclic permutation of 1, 2, and 3. Perimetric coordinates have the great advantage of being independent over their range from 0 to  $\infty$  unlike the interparticle coordinates, which are connected by the triangular condition and thus have dependent domains. The resulting Schrödinger equation is solved using a series solution method by expanding the wavefunction in a triple orthogonal set of Laguerre functions<sup>27</sup> in scaled perimetric coordinates

$$\psi(z_1, z_2, z_3) = e^{-\frac{1}{2}(\alpha z_1 + \beta z_2 + \gamma z_3)} \times \sum_{l,m,n=0}^{\infty} A(l, m, n) L_l(\alpha z_1) L_m(\beta z_2) L_n(\gamma z_3). \quad (4)$$

This results in a 57-term recursion relation between the coefficients, which is used to form a sparse secular determinant that is solved in truncated form to give the eigenvalues as a function of basis set size  $N$ .

Initially, as in previous work,<sup>25</sup> the energy  $E$  is removed from the Schrödinger equation by the relation

$$E = -K\varepsilon^2 \quad (5)$$

and the nonlinear scale parameter  $K$  is used variationally to improve convergence compared to the work of Pekeris<sup>27</sup> who took  $K = 1$ . Setting  $\alpha = \beta = \varepsilon$  and  $\gamma = \alpha + \beta$  reduces the exponent in the wave function (4) to

$$(\alpha z_1 + \beta z_2 + \gamma z_3) = 2\varepsilon(r_1 + r_2) = \left(\frac{2}{\sqrt{K}}\right) \sqrt{-E}(r_1 + r_2).$$

When  $K = 1$  this, in principle, is an exact form as it contains the correct asymptotic behaviour of the solution of the Schrödinger equation for two-electron atoms and ions at large  $r_1$  and  $r_2$ .<sup>28</sup> Although this works very well for atomic-like systems (with one heavy mass)<sup>23,25</sup> and systems where all masses are similar (e.g.,  $\text{Ps}^-$ )<sup>29</sup> convergence for molecule-like systems (with two heavy masses) is very slow. Arias de Saavedra *et al.*<sup>30</sup> have addressed this problem by ensuring an explicit dependence on  $r_{12}(=r_3)$  in the exponential behaviour at large

$r$ , but do not include the energy parameter in their definition of the scaled perimetric coordinates. This explicit dependence on  $r_3$  is achieved by relaxing the constraint  $\alpha + \beta = \gamma$ , i.e.,  $\alpha(= \beta)$  and  $\gamma$  are varied independently. However, if the constraint  $\alpha = \beta$  is also relaxed, then for symmetric systems with fermionic exchange the useful quasi-orthogonal character of the wavefunction is lost. Therefore, in this work which involves such systems, the condition  $\alpha = \beta$  was imposed, and then either  $\gamma = 2\alpha$  or no constraint was put on  $\gamma$ ; for non-symmetric systems, i.e., non-identical particles, the variation of all three nonlinear parameters has also been implemented.

The nonlinear variational parameters were optimised using the conjugate gradient method in order to minimise the energy.<sup>31</sup> However, for non-atomic systems with two nonlinear parameters ( $\alpha, \gamma$ ) it was necessary to first perform a scan of the parameters due to the potential for multiple minima. When the calculation included the energy parameter  $\varepsilon$  in the coordinates, and the electron was not the lightest mass, it was necessary either to scale the energy parameter by the mass of the lightest particle directly or to set the mass of the lightest particle to 1 (e.g., use muonic units). The masses for all the systems considered were taken from CODATA<sup>32</sup> and are provided in Table I.

## III. RESULTS

### A. Energy convergence

Table II shows the performance of the basis sets with one and with two nonlinear parameters and the effect of including the energy parameter  $\varepsilon$  in the coordinates for  $\text{H}^-$  ( $e^- e^- p^+$ ),  $\text{Mu}^-$  ( $e^- e^- \mu^+$ ),  $\mu\text{H}^-$  ( $\mu^- \mu^- p^+$ ),  $\text{Ps}^-$  ( $e^- e^- e^+$ ),  $\mu\text{D}_2^+$  ( $d^+ d^+ \mu^-$ ),  $\text{Mu}_2^+$  ( $\mu^+ \mu^+ e^-$ ),  $\text{H}_2^+$  ( $p^+ p^+ e^-$ ), and  $\text{D}_2^+$  ( $d^+ d^+ e^-$ ). These were chosen as their mass ratios ( $m_1/m_3$ ) vary from  $5.446 \times 10^{-4}$  to  $3.670 \times 10^3$ . The masses of all the particles are included from the beginning in each calculation. This is highly advantageous as the mass-polarisation effects, for example, are automatically included and thus determined to a precision limited only by that of the physical constants. However, it does mean that any redetermination of the fundamental constants changes the precision of the energy obtained suggesting that energies should be recalculated with the new values. In this work, the latest CODATA values are used.<sup>32</sup> In Table II, numbers reported in the literature that go beyond the precision of the masses used in this work are given in italics (and truncated).

As observed previously,<sup>25,29,30,33</sup> the increase in the rate of convergence for atomic systems and for exotic two-electron systems ( $\text{Ps}^-$  and  $\text{Mu}^-$ ) is insignificant when a second nonlinear variational parameter is included. However, for systems with molecular character (such as  $\text{H}_2^+$ ) the second nonlinear parameter is vital for reasonable convergence. This is due to the importance of having an adequate description of the interparticle distribution between the two heavier particles. Even then, the molecular-type systems (such as  $\text{H}_2^+$  and  $\text{D}_2^+$ ) converge more slowly than the atomic systems. For all, even the atomic systems, inclusion of the energy parameter in the description of the asymptotic behaviour is of no particular benefit. In the work that follows, a methodology that is suitable for

TABLE II. Study of the rate of energy convergence for a 1078-term wave function where  $0-\varepsilon$  = the wave function contains the energy parameter  $\varepsilon$  and  $K = 1$ ,  $1-\varepsilon$  = the energy parameter  $\varepsilon$  and  $K$  is varied,  $1 =$  one nonlinear variational parameter, and  $2 =$  two nonlinear variational parameters; these are compared with the results from a 2856-term wave function (parameters not scanned to optimise) and the best literature values (truncated to 12 s.f.; numbers in italics are not comparable to the present work due to differences in the mass used). The energies for  $\mu\text{H}^-$  and  $\mu\text{D}_2^+$  are given in muonic atomic units.

$N$	Basis	$\text{H}^- (\text{e}^- \text{e}^- \text{p}^+)$	$\text{Mu}^- (\text{e}^- \text{e}^- \mu^+)$	$\mu\text{H}^- (\mu^- \mu^- \text{p}^+)$	$\text{Ps}^- (\text{e}^- \text{e}^- \text{e}^-)$
		$m_1/m_3 = 5.446 \times 10^{-4}$	$m_1/m_3 = 4.836 \times 10^{-3}$	$m_1/m_3 = 1.126 \times 10^{-1}$	$m_1/m_3 = 1.000$
1078	$0-\varepsilon$	-0.527 445 879 971	-0.525 054 805 419	-0.471 866 335 351	-0.262 005 070 179
	$1-\varepsilon$	-0.527 445 880 856	-0.525 054 806 285	-0.471 866 335 351	-0.262 005 070 179
	1	-0.527 445 880 308	-0.525 054 806 257	-0.471 866 335 439	-0.262 005 070 183
	2	-0.527 445 880 936	-0.525 054 806 359	-0.471 866 335 829	-0.262 005 070 181
2856	2	-0.527 445 881 063	-0.525 054 806 510	-0.471 866 336 008	-0.262 005 070 191
Literature		-0.527 445 881 109 <sup>a</sup>	-0.525 054 806 243 <sup>b</sup>	0.471 866 3476 <sup>c</sup>	-0.262 005 070 232 <sup>d</sup>
$N$	Basis	$\mu\text{D}_2^+ (\text{d}^+ \text{d}^+ \mu^-)$	$\text{Mu}_2^+ (\mu^+ \mu^+ \text{e}^-)$	$\text{H}_2^+ (\text{p}^+ \text{p}^+ \text{e}^-)$	$\text{D}_2^+ (\text{d}^+ \text{d}^+ \text{e}^-)$
		$m_1/m_3 = 1.775 \times 10$	$m_1/m_3 = 2.068 \times 10^2$	$m_1/m_3 = 1.836 \times 10^3$	$m_1/m_3 = 3.670 \times 10^3$
1078	$0-\varepsilon$	-0.531 111 108 795	-0.584 634 830 218	-0.593 491 412 007	-0.594 147 283 314
	$1-\varepsilon$	-0.531 111 130 226	-0.585 125 619 750	-0.596 934 608 385	-0.598 301 359 076
	1	-0.531 111 130 227	-0.585 125 619 884	-0.596 934 608 385	-0.598 301 404 265
	2	-0.531 111 130 229	-0.585 126 098 252	-0.597 139 019 182	-0.598 787 112 904
2856	2	-0.531 111 130 229	-0.585 126 098 252	-0.597 139 063 079	-0.598 788 784 032
Literature		-0.531 111 132 193 <sup>e</sup>	-0.585 126 097 219 <sup>f</sup>	-0.597 139 063 123 <sup>g</sup>	-0.598 788 784 331 <sup>h</sup>

<sup>a</sup>Reference 33.

<sup>b</sup>Reference 40.

<sup>c</sup>Reference 39.

<sup>d</sup>Reference 44.

<sup>e</sup>Reference 41.

<sup>f</sup>Reference 30.

<sup>g</sup>Reference 42.

<sup>h</sup>Reference 43.

a range of symmetric, possibly unknown, systems is required and so the remainder of the data presented was obtained using a wave function with two nonlinear variational parameters, as this methodology was suitable for both atomic- and molecular-type systems.

The least accurate mass value used is known to 6 significant figures (s.f.), see Table I, thus all energies are converged and presented to at least 6 s.f. Typically, this level of convergence was achieved using either a 1078-term or a 1925-term wave function with two nonlinear variational parameters. In general, a full scan of the parameters followed by an optimisation at the minimum was performed at  $N = 1078$  and/or  $N = 1925$  followed by an optimisation at  $N = 2856$  to determine the level of convergence.

## B. Stability criteria

The ground state energy of a wide-range of symmetric systems of the form  $\{m_1^\pm m_2^\pm m_3^\mp\}$  were calculated in a series ranging from  $\{(m_1 = m_2) \gg (m_3 = 1)\}$  to  $\{m_3 \gg (m_1 = m_2 = 1)\}$ . For consistency, the charges on each particle were set as  $\{m_1^- m_2^- m_3^+\}$ , although reversing the charges would produce the same  $E_0$  due to charge inversion invariance. The calculated energies for all the systems considered are given in Table III. To determine the stability of three-body systems, the lowest energy threshold is considered. In the case of three unit charges  $\{m_1^\pm m_2^\pm m_3^\mp\}$ , if we assume that  $m_1 \geq m_2$ , then the system will break up into  $\{m_1^\pm m_3^\mp\}$  (as the heavier bound pair will have a greater energy due to the dependence on reduced mass) and an isolated particle  $\{m_2^\pm\}$  at rest at infinity.<sup>21</sup> Therefore, the threshold energy of the three-particle system

coincides with the ground-state energy of the two-body atom, which is simply the ground state energy of the hydrogen-like atom consisting of particles 1 and 3, i.e.,

$$E_{th} = E(m_1, m_3) = -\frac{1}{2}\mu_{13} = -\frac{1}{2} \frac{m_1 m_3}{m_1 + m_3}. \quad (6)$$

Thus, the stability limit depends only on the ratio of the masses, and not their absolute values, and in this work given that  $m_1 = m_2$ , it depends only on  $m_1/m_3$ . Following the work of Martin *et al.*,<sup>13</sup> the stability of each system is measured in terms of  $g$  a dimensionless ratio of the ground state energy of the three-body system ( $E_0$ ) and the threshold energy ( $E_{th}$ ):

$$g = \frac{E_0 - E_{th}}{E_{th}}. \quad (7)$$

## C. The function $g(a_3)$

A plot of  $g$  against  $a_3$  for a range of symmetric systems yields the graph depicted in Figure 2(a). Particularly interesting is that  $g(a_3)$  does not decrease monotonically to  $a_3 = 0$  corresponding to  $\infty\text{H}^-$ , but contains a minimum. Based on the data in Table III, this minimum is estimated to occur at  $a_3 \approx 0.2$  which corresponds to the system  $(\text{p}, \text{p}, \text{d})^\pm$ , with a mass ratio of  $\approx 0.5$ . To investigate this further, the data points listed in Table III and seven additional points having  $a_3$  values between the data points  $(\tau, \tau, \text{t})^\pm$  and  $(\text{p}, \text{p}, \text{t})^\pm$  in increments of 0.01, were fitted to a functional form, and the function differentiated to determine the minimum as accurately as possible.

Previously, Martin *et al.*<sup>13</sup> described  $g(a_3)$  as having a square-root behaviour near  $a_3 = 1$ . By simply adding a

TABLE III. Total energy (in electron atomic units), mass ratio ( $m_1/m_3$ ), reciprocal mass of the uniquely charged particle ( $a_3$ ), and relative excess binding energy ( $g$ ), for some symmetric configurations of the form  $\{m_1^+ m_1^+ m_3^-\}$ .

System	Energy (a.u.)	$m_1/m_3$	$a_3$	$g$
(t, t, e)	-0.599 506 (9)	$5.496\,922 \times 10^3$	0.999 636 292	0.199 231 931
(d, d, e)	-0.598 788 7(8)	$3.670\,483 \times 10^3$	0.999 455 409	0.197 903 841
( $\tau$ , $\tau$ , e)	-0.598 680 (5)	$3.477\,500 \times 10^3$	0.999 425 147	0.197 705 365
(p, p, e)	-0.597 139 06(3)	$1.836\,153 \times 10^3$	0.998 911 951	0.194 928 550
( $\mu$ , $\mu$ , e)	-0.585 126 098 252 (3)	$2.067\,683 \times 10^2$	0.990 420 001	0.175 911 924
(t, t, $\mu$ )	-112.972 860 407 (5)	$2.658\,494 \times 10$	0.930 033 077	0.133 852 490
(d, d, $\mu$ )	-109.816 937 170 (1)	$1.775\,167 \times 10$	0.898 742 754	0.122 060 128
( $\tau$ , $\tau$ , $\mu$ )	-109.331 147 (4)	$1.681\,665 \times 10$	0.893 711 158	0.120 408 873
(11.3, 11.3, 1)	-0.508 912 277 502 (5)	11.3	0.85	0.107 897 524
(p, p, $\mu$ )	-102.223 512 95(5)	8.880 243	0.816 180 581	0.100 118 955
(6,6,1)	-0.466 087 497 252 (4)	6.0	0.75	0.087 537 494
(4.7, 4.7, 1)	0.445 261 313 47(2)	4.7	0.70	0.079 995 526
(3.7, 3.7, 1)	-0.422 360 557 1(8)	3.7	0.65	0.073 024 118
(t, t, p)	-734.528 908 (0)	2.993 717	0.599 496 730	0.067 324 900
(2.4, 2.4, 1)	-0.374 811 142 2(6)	2.4	0.55	0.061 964 903
(d, d, p)	-647.474 58(4)	1.999 008	0.499 875 907	0.058 052 104
( $\tau$ , $\tau$ , p)	-635.051 59(5)	1.893 715	0.486 351 733	0.056 991 143
(t, t, $\tau$ )	-1122.214 356 (7)	1.580 870	0.441 476 486	0.053 785 891
(t, t, d)	-1158.683 72(8)	1.497 602	0.428 179 601	0.052 927 693
(d, d, $\tau$ )	-936.125 280 (9)	1.055 601	0.345 464 277	0.048 526 850
( $\tau$ , $\tau$ , $\tau$ )	-911.030 929 (9)	1.0	0.333 333 333	0.048 020 281
(t, t, t)	-1440.221 310 (6)	1.0	0.333 333 333	0.048 020 281
(e, e, e)	-0.262 005 070 (2)	1.0	0.333 333 333	0.048 020 281
( $\mu$ , $\mu$ , $\mu$ )	-54.174 338 8(4)	1.0	0.333 333 333	0.048 020 281
(p, p, p)	-481.081 309 (8)	1.0	0.333 333 333	0.048 020 281
(d, d, d)	-961.685 14(7)	1.0	0.333 333 333	0.048 020 281
( $\tau$ , $\tau$ , d)	-935.260 851 (6)	$9.473\,276 \times 10^{-1}$	0.321 419 184	0.047 558 671
(d, d, t)	-1150.610 15(2)	$6.677\,343 \times 10^{-1}$	0.250 300 147	0.045 591 012
( $\tau$ , $\tau$ , t)	-1113.316 616 (6)	$6.325\,632 \times 10^{-1}$	0.240 284 132	0.045 430 702
(p, p, $\tau$ )	-627.929 516 (9)	$5.280\,625 \times 10^{-1}$	0.208 880 332	0.045 137 029
(p, p, d)	-639.557 763 (2)	$5.002\,482 \times 10^{-1}$	0.200 079 431	0.045 115 069
(p, p, t)	-719.649 17(3)	$3.340\,329 \times 10^{-1}$	0.143 114 052	0.045 703 543
(1, 1, 5)	-0.436 497 014 6(9)	0.2	0.09	0.047 592 835
( $\mu$ , $\mu$ , p)	-97.566 992 7(1)	$1.126\,095 \times 10^{-1}$	0.053 303 521	0.050 005 962
( $\mu$ , $\mu$ , $\tau$ )	-102.672 896 (1)	$5.946\,487 \times 10^{-2}$	0.028 873 944	0.052 176 133
( $\mu$ , $\mu$ , d)	-102.991 920 (9)	$5.633\,272 \times 10^{-2}$	0.027 394 749	0.052 325 179
( $\mu$ , $\mu$ , t)	-104.944 126 (2)	$3.761\,529 \times 10^{-2}$	0.018 460 446	0.053 272 073
(e, e, $\mu$ )	-0.525 054 806 (5)	$4.836\,332 \times 10^{-3}$	0.002 412 332	0.055 188 291
(e, e, p)	-0.527 445 881 (0)	$5.446\,170 \times 10^{-4}$	0.000 272 234	0.055 466 274
(e, e, $\tau$ )	-0.527 589 83(7)	$2.875\,918 \times 10^{-4}$	0.000 143 775	0.055 483 136
(e, e, d)	-0.527 598 32(4)	$2.724\,437 \times 10^{-4}$	0.000 136 203	0.055 484 131
(e, e, t)	-0.527 649 0(4)	$1.819\,200 \times 10^{-4}$	0.000 090 952	0.055 490 076
$\infty\text{H}^-$	-0.527 751 01(6)	0.0	0.0	0.055 502 033

quadratic term, it is possible to model the behaviour of the function as  $a_3$  decreases, resulting in the form

$$g(a_3) = A - B\sqrt{1 - a_3} + C(1 - a_3)^2. \quad (8)$$

The parameters  $A$ ,  $B$ , and  $C$  are optimised by fitting to the 36 distinct finite-mass symmetric systems (listed in Table III), along with some additional hypothetical mass systems, yielding the values  $A = 0.200\,907$ ,  $B = 0.237\,411$ , and  $C = 0.091\,054$ . This produces a function with a reasonably good fit to the data, and a  $R^2$  value of 0.998. However, a fit commensurate with the level of accuracy of the calculated

data requires a more flexible function

$$g(a_3) = \sum_{i=0}^{2n} c_i (1 - a_3)^{\frac{i}{2}}. \quad (9)$$

Taking this expansion to fifth order ( $n = 5$ ) results in an excellent fit with a  $R^2$  value of 0.999 999 980, Figure 2(b). The optimised values for this fit are:  $c_0 = 0.588\,641\,277$ ,  $c_1 = 0.326\,670\,402$ ,  $c_2 = 0.383\,300\,517$ ,  $c_3 = 2.048\,690\,70$ ,  $c_4 = 12.366\,541\,0$ ,  $c_5 = 46.866\,686\,5$ ,  $c_6 = 110.492\,237$ ,  $c_7 = 162.933\,845$ ,  $c_8 = 146.384\,326$ ,  $c_9 = 73.345\,924\,6$ , and  $c_{10} = 15.745\,569\,2$ . Differentiating the function  $g(a_3)$  to determine the minimum provides the symmetric system that has

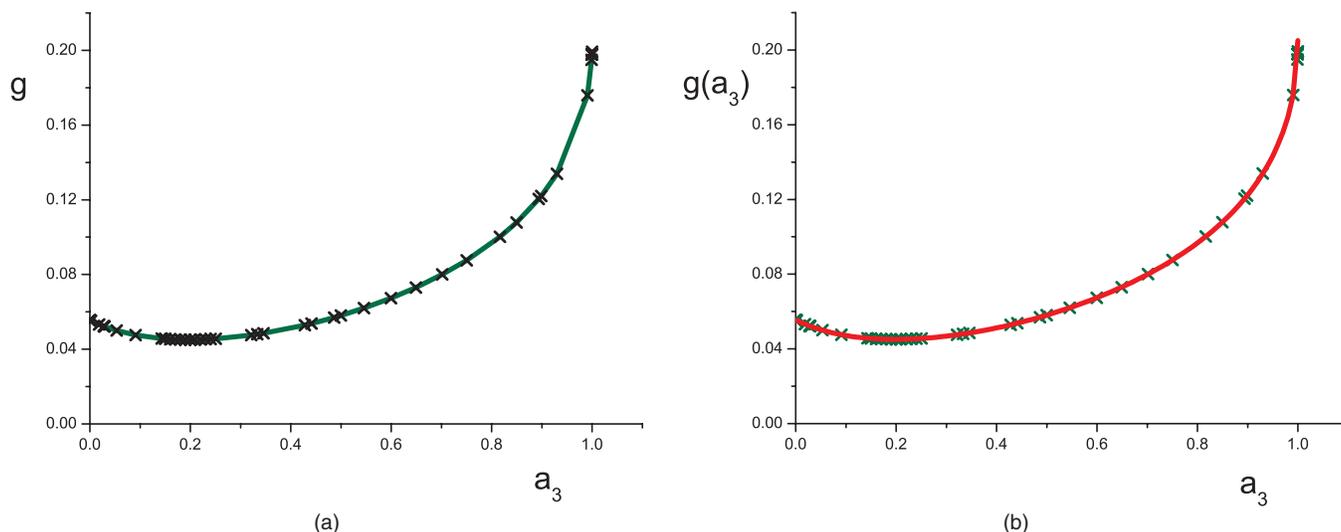


FIG. 2. (a) Plot of  $g$  against  $a_3$  for a range of symmetric systems, (b) the function  $g(a_3)$  (red line) compared with the raw data of  $g$  versus  $a_3$  (green crosses).

the least fractional binding energy gained by association with a third particle. However, the minimum is sensitive to the functional form and so additional data points were calculated about the minimum to estimate the accuracy. Based on this analysis, and comparing with alternative functional forms, the minimum is estimated to occur at  $a_3 = 0.197 \pm 0.001$ , corresponding to the system ( $m_1 = m_2 = 1$ ,  $m_3 = 2.04 \pm 0.01$ ) which has a mass ratio of  $m_1/m_3 = 0.491 \pm 0.003$ .

#### D. The stability band width $\delta$

Using the  $g$  values directly, or from the parameterised function  $g(a_3)$ , the lower bound of  $\delta(a_3)$  can be calculated using (3) for each  $a_3$  value and the results presented on a mass fraction ternary diagram (Figure 3). From the stability zone in Figure 3 (solid shading/blue), it can be deduced that all systems inside this (solid shading/blue) region are stable with respect to dissociation and therefore contain at least one bound state. The stability zone saturates the sides of the ternary diagram at  $a_3 = 0.8292 \pm 0.0001$ , corresponding to ( $m_1 = \infty$ ,  $m_2 = 4.854 \pm 0.003$ ,  $m_3 = 1$ ), and the lower limit of the stability band at  $a_3 = 0$  corresponds to a mass ratio  $m_1/m_2 = 1.111 \pm 0.001$ , i.e., ( $m_1 = 1.111$ ,  $m_2 = 1$ ,  $m_3 = \infty$ ). However, because  $\delta(a_3)$  is a lower bound, the stability region may be larger. For example, the system  $d^+ t^+ p^-$ , consisting of a deuteron, triton, and anti-proton lies just outside the calculated stability zone, however this species is predicted to have a weakly bound ground state.<sup>34–36</sup> Additionally, literature values indicate that the minimum mass required to bind a “positron” to a hydrogen atom with an infinite nuclear mass is between  $1.51 m_e$ ,<sup>15</sup> and  $2.20 m_e$ ,<sup>14</sup> whereas our results suggest that a mass of  $4.85 m_e$  would be required. The inaccuracy in the present result is due to underestimation of the width of the stability band. The lower limit of the stability band (3) is derived by rewriting the Hamiltonian as a sum of symmetric terms (symmetric under  $1 \leftrightarrow 2$  exchange) and anti-symmetric terms, and then applying the variational principle to this Hamiltonian using the symmetric ground state of the symmetric Hamiltonian as a trial wave function.<sup>13,22</sup>

This underestimate would indicate that the anti-symmetric (symmetry-breaking) terms are not small.<sup>37</sup> Clearly, a more accurate value could be obtained by solving the Schrödinger equation for three unequal mass particles directly.<sup>38</sup> Further work will involve using a method to predict a more precise bound based on determining the value of the third particle mass that corresponds to the critical binding energy, i.e., when  $E_0 = E_{th}$ .

Particularly interesting is the mass ratio of the system which corresponds to the minimum in the function  $g(a_3)$  as  $Ps^-$  ( $m_1 = m_2 = m_3 = 1$ ) actually possesses the smallest value of  $E_0 - E_{th}$  and thus has the smallest magnitude of energy gain due to the presence of a third particle. However, it does not possess the least fractional gain as defined by  $g$ ; nor is  $g(a_3)$  minimal for  $a_3 = 0$  which would correspond to  $\infty H^-$ .<sup>22</sup> This determination is, to our knowledge, the most accurate to

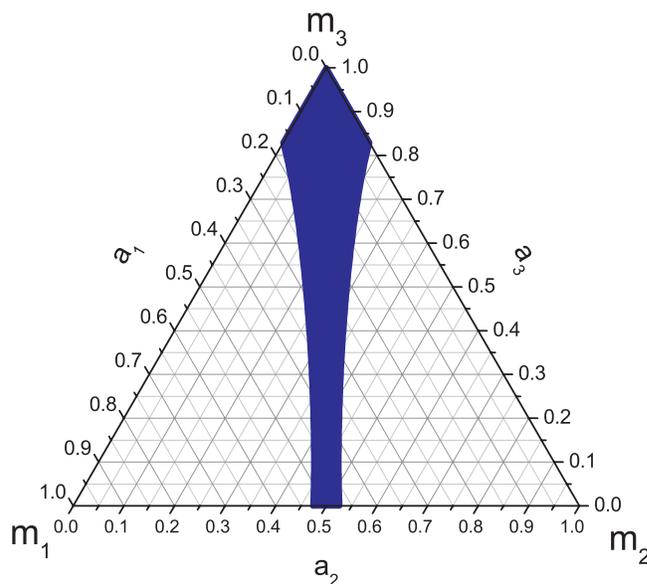


FIG. 3. The stability domain (solid shading/blue) derived from the binding energies of the systems along the symmetry axis.

date. Moreover, a recent study into the emergence of molecular structure in Coulombic three-particle systems considered the distribution of the identical particles in the ground state and concluded that a node in the particle density at the centre of mass first appears when  $0.4 < m_1/m_3 < 0.8$ .<sup>6</sup> It is suggested that such a transition in density distribution could determine the crossover point between molecular and atomic behaviour. The results presented here, suggest that this cross-over point causes a destabilisation and thus corresponds to the system with the least fractional gain in binding energy by association with a third particle.

#### IV. CONCLUSIONS

In this paper, we have unified the treatment of “atomic” and “molecular” type systems by solving the Schrödinger equation for three-particle systems in translation-free internal coordinates using a wave function expanded in a triple orthogonal set of Laguerre functions with two nonlinear parameters. A range of symmetric unit-charge systems have been calculated to high accuracy and used to predict the width of the stability band in terms of the fractional additional binding  $g$  as a function of the reciprocal mass of the uniquely charged particle,  $a_3$ , using the method of Martin *et al.*<sup>13</sup> A functional form of  $g(a_3)$  is obtained by fitting to these data and is used to determine the minimum value of  $g(a_3)$ , the point of least relative excess binding due to a third particle. The minimum is estimated to occur at  $m_1/m_3 = 0.491$  which corresponds to ( $m_1 = m_2 = 1, m_3 = 2.04$ ). Mátyus *et al.*<sup>6</sup> discuss the emergence of molecular structure in three-particle systems in terms of the density at the centre of mass and calculate that the transition takes place within the interval  $0.4 < m_1/m_3 < 0.8$ ; the results presented here indicate that the transition from atomic-like to molecular-like behaviour occurs when the system has the least energetic gain by association with the third particle.

#### ACKNOWLEDGMENTS

The authors would like to thank the University of Sussex for financial support and Professor B. T. Sutcliffe and Professor A. J. McCaffery for reading the paper before publication.

<sup>1</sup>See, for example, some of our recent applications L. Ma, T. Takashima, J. Koka, H. J. Kimber, H. Cox, and A. J. Stace, *J. Chem. Phys.* **138**, 164301 (2013); G. Roffe and H. Cox, *J. Phys. Chem. A* **117**, 3017 (2013); G. D. C. Aitken, H. Cox, and A. J. Stace, *ibid.* **116**, 3035 (2012); H. Stewart, G. Wu, L. Ma, M. Barclay, A. D. Vieira, A. King, H. Cox, and A. J. Stace, *ibid.* **115**, 6948 (2011); H. Cox, C. Norris, G. Wu, J. Guan, S. Hessey, and A. J. Stace, *Dalton Trans.* **40**, 11200, (2011); L. Ferro, P. B. Hitchcock, M. P. Coles, H. Cox, and J. R. Fulton, *Inorg. Chem.* **50**, 1879 (2011).  
<sup>2</sup>G. Wu, C. Norris, H. Stewart, H. Cox, and A. J. Stace, *Chem. Commun.* **35**, 4153 (2008); H. Cox and A. J. Stace, *Int. Rev. Phys. Chem.* **29**, 555 (2010).

<sup>3</sup>L. S. Cederbaum, *J. Chem. Phys.* **138**, 224110 (2013).  
<sup>4</sup>B. T. Sutcliffe and R. G. Woolley, *J. Chem. Phys.* **137**, 22A544 (2012); B. T. Sutcliffe, *Theor. Chem. Acc.* **118**, 563 (2007).  
<sup>5</sup>J. W. Hollett and P. M. W. Gill, *J. Chem. Phys.* **134**, 114111 (2011); P.-F. Loos and P. M. W. Gill, *ibid.* **132**, 234111 (2010); **138**, 164124 (2013).  
<sup>6</sup>E. Mátyus, J. Hutter, U. Müller-Herold, and M. Reiher, *Phys. Rev. A* **83**, 052512 (2011).  
<sup>7</sup>M. J. G. Peach, A. M. Miller, A. M. Teale, and D. J. Tozer, *J. Chem. Phys.* **129**, 064105 (2008).  
<sup>8</sup>S. E. Jones, *Nature (London)* **321**, 127 (1986).  
<sup>9</sup>K. Ishida, K. Nagamine, T. Matsuzaki, and N. Kawamura, *Nucl. Phys. B, Proc. Suppl.* **149**, 348 (2005).  
<sup>10</sup>D. Balin *et al.*, *Phys. Part. Nucl.* **42**, 185 (2011).  
<sup>11</sup>J.-P. Karr and L. Hilico, *Phys. Rev. Lett.* **109**, 103401 (2012).  
<sup>12</sup>R. C. Vilão, J. M. Gil, A. Weidinger, H. V. Alberto, J. Piroto Duarte, B. F. O. Costa, N. Ayres de Campos, R. L. Lichti, K. H. Chow, S. P. Cottrell, and S. F. J. Cox, *Physica B* **404**, 888 (2009).  
<sup>13</sup>A. Martin, J.-M. Richard, and T. T. Wu, *Phys. Rev. A* **46**, 3697 (1992).  
<sup>14</sup>M. Rotenberg and J. Stein, *Phys. Rev.* **182**, 1 (1969).  
<sup>15</sup>E. A. G. Armour and D. M. Schrader, *Can. J. Phys.* **60**, 581 (1982).  
<sup>16</sup>R. D. Poshusta, *J. Phys. B* **18**, 1887 (1985).  
<sup>17</sup>A. M. Frolov and D. M. Bishop, *Phys. Rev. A* **45**, 6236 (1992).  
<sup>18</sup>T. K. Rebane and A. V. Filinsky, *Phys. At. Nucl.* **65**, 41 (2002).  
<sup>19</sup>T. K. Rebane and A. A. Kuzminskii, *Opt. Spectrosc.* **93**, 833 (2002).  
<sup>20</sup>D. K. Gridnev, C. Greiner, and W. Greiner, *J. Math. Phys.* **46**, 052104 (2005).  
<sup>21</sup>E. A. G. Armour and W. Byers Brown, *Acc. Chem. Res.* **26**, 168 (1993).  
<sup>22</sup>E. A. G. Armour, J.-M. Richard, and K. Varga, *Phys. Rep.* **413**, 1 (2005).  
<sup>23</sup>H. Cox, S. J. Smith, and B. T. Sutcliffe, *Phys. Rev. A* **49**, 4520 (1994).  
<sup>24</sup>R. N. Hill, *J. Math. Phys.* **18**, 2316 (1977).  
<sup>25</sup>H. Cox, S. J. Smith, and B. T. Sutcliffe, *Phys. Rev. A* **49**, 4533 (1994).  
<sup>26</sup>A. S. Coolidge and H. M. James, *Phys. Rev.* **51**, 855 (1937).  
<sup>27</sup>C. L. Pekeris, *Phys. Rev.* **112**, 1649 (1958).  
<sup>28</sup>E. A. Hylleraas, *Z. Phys.* **54**, 347 (1929); for an English translation see H. Hetttema, *Quantum Chemistry: Classic Scientific Papers* (World Scientific Publishing, Singapore, 2000), p. 104.  
<sup>29</sup>H. Cox, P. E. Sinclair, S. J. Smith, and B. T. Sutcliffe, *Mol. Phys.* **87**, 399 (1996).  
<sup>30</sup>F. Arias de Saavedra, E. Buendía, F. J. Gálvez, and A. Sarsa, *Eur. Phys. J. D* **2**, 181 (1998).  
<sup>31</sup>W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical Recipes: The Art of Scientific Computing*, 3rd ed. (Cambridge University Press, New York, 2007).  
<sup>32</sup>P. J. Mohr, B. N. Taylor, and D. B. Newell, *Rev. Mod. Phys.* **84**, 1527 (2012); these data can also be found at [physics.nist.gov/constants](http://physics.nist.gov/constants).  
<sup>33</sup>F. Arias de Saavedra, E. Buendía, F. J. Gálvez, and A. Sarsa, *Eur. Phys. J. D* **13**, 201 (2001).  
<sup>34</sup>A. M. Frolov and A. J. Thakkar, *Phys. Rev. A* **46**, 4418 (1992).  
<sup>35</sup>D. M. Bishop, A. M. Frolov, and V. H. Smith, Jr., *Phys. Rev. A* **51**, 3636 (1995).  
<sup>36</sup>A. M. Frolov, *J. Phys. B* **46**, 125001 (2013).  
<sup>37</sup>V. Korobov and J.-M. Richard, *Phys. Rev. A* **71**, 024502 (2005).  
<sup>38</sup>A. A. Frost, M. Inokuti, and J. P. Lowe, *J. Chem. Phys.* **41**, 482 (1964).  
<sup>39</sup>S. Bhattacharyya, J. H. Saha, P. K. Mukherjee, and T. K. Mukherjee, *Phys. Scr.* **85**, 065305 (2012).  
<sup>40</sup>A. M. Frolov, *Phys. Rev. A* **69**, 022505 (2004).  
<sup>41</sup>A. M. Frolov, *Eur. Phys. J. D* **66**, 212 (2012).  
<sup>42</sup>D. H. Bailey and A. M. Frolov, *J. Phys. B* **35**, 4287 (2002).  
<sup>43</sup>L. Hilico, N. Billy, B. Grémaud, and D. Delande, *Eur. Phys. J. D* **12**, 449 (2000).  
<sup>44</sup>A. M. Frolov, *Phys. Rev. A* **60**, 2834 (1999).