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# Two-electron atoms, ions, and molecules

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The quantum mechanics of two-electron systems is reviewed, starting with the ground state of the helium atom and heliumlike ions with central charge Z. The case of $Z \geq 2$ is rather straightforward. In contrast, for negative hydrogen ion with $Z = 1$, the stability of H$^-$ cannot be achieved using a product of individual electron wavefunctions and requires explicit account of the anticorrelation among the two electrons. The wavefunction proposed by Chandrasekhar is revisited, where the permutation symmetry is first broken and then restored by a counterterm. More difficult problems can be studied using the same strategy such as the stability of hydrogenlike ions for any value of the proton-to-electron mass ratio $M/m$, the energy of the lowest spin-triplet state of helium and heliumlike ions, and the stability of the doubly excited hydrogen ion with unnatural parity. The positronium molecule, which was predicted years ago and discovered recently, can also be shown to be stable against spontaneous dissociation. Emphasis is placed on symmetry breaking, which can either spoil or improve the stability. © *2010 American Association of Physics Teachers.*
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## I. INTRODUCTION

The discussion of two-electron atoms or ions is of much importance when teaching quantum mechanics and provides an opportunity to discuss the transition from simple binary systems to more complicated structures, with applications of perturbation theory and variational methods.

Understanding two-electron atoms was crucial to show that quantum mechanics was not just an ansatz, which works fortuitously for the hydrogen atom. Although the Bohr–Sommerfeld quantization method accounts for one-electron atoms, it faced serious difficulties for the description of helium. Then Heisenberg[1] and others[2] showed that the helium atom can be well described in the framework of the new quantum mechanics.

Binding two electrons to a helium nucleus or to a heavier nucleus with charge $Z \geq 2$ is obvious because the first attached electron leaves a positively charged kernel that easily traps the second electron. The problem is to accurately calculate the energy spectrum and the associated wavefunctions and not to demonstrate the existence of bound states. It is thus unfortunate that the discussion in many textbooks, even the best ones, is restricted to helium and does not consider the more challenging case of $Z = 1$, that is, the negative hydrogen ion. Noticeable exceptions are Refs. 3–6.

The negative hydrogen ion, H$^-$, enters a variety of physical, chemical, biological, and geological processes.[7,8] In astrophysics, it plays a role at the Sun's surface, and its absorption and emission properties have been studied by Chandrasekhar.[9] Intense beams of H$^-$ are foreseen for future nuclear-fusion devices.[10] It is the simplest prototype of a fragile structure at the edge between binding and nonbinding and cannot be described by simple approximations such as Hartree wavefunctions, even though the latter accounts for the properties of well-bound systems. Other examples are atomic clusters made of noble-gas atoms and Borromean nuclei with two weakly bound peripheral neutrons. (A Borromean system is bound, although its subsystems are unstable. For instance, $^5$He$=(\alpha, n)$ and $(n, n)$ is not bound, but $^6$He$=(\alpha, n, n)$ is stable against any dissociation and relies only on $\beta$ decay to disintegrate.)

Intimately related to H$^-$ is the positronium molecule Ps$_2$ of content $(e^+, e^+, e^-, e^-)$, predicted in 1945 by Wheeler[11] and discovered only recently.[12] Demonstrating its stability against dissociation into two positronium atoms can be done by a generalization of the Chandrasekhar wavefunction, although the calculation becomes slightly more intricate. This molecule has many symmetries. It can be seen that breaking particle identity and breaking charge conjugation have dramatically different effects on its stability. In the former case, it quickly disappears, and in the latter case, it is reinforced. In particular, the stability of the hydrogen molecule can be, somewhat paradoxically, demonstrated as a consequence of the stability of the positronium molecule. This approach to the hydrogen molecule from the positronium molecule is at variance with the more physical starting point of two infinitely massive protons but illustrates the importance of symmetry breaking.

This paper reviews what can be taught about the quantum mechanics of two-electron atoms and molecules at the introductory and more advanced level. We begin in Sec. II with the ground state of two-electron atoms and ions, which is a spin-singlet configuration. The easiest case of a central charge $Z \geq 2$ is briefly reviewed. We then discuss the more difficult hydrogen ion with $Z = 1$. We focus on the beautiful solution proposed by Chandrasekhar,[13] which is a product of single-electron wavefunctions with different range parameters, supplemented by a counterterm in which the two electrons are interchanged, so that the overall permutation sym-

metry is restored. Two other examples of heliumlike systems are presented in Sec. III, the lowest spin-triplet state, whose orbital wavefunction is antisymmetric, and the unnatural parity state of the hydrogen ion, which is very loosely bound below its threshold. In Sec. IV the positronium molecule is discussed, as well as some of its less symmetric variants. After a brief summary in Sec. V, some details about the calculation of the matrix elements are given in the Appendix.

## II. THE GROUND STATE OF TWO-ELECTRON ATOMS AND IONS

We first consider the nonrelativistic Hamiltonian describing two electrons of mass $m$ and charge $e$ around a fixed charged $Ze$,

$$H = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r_{12}}, \tag{1}$$

with $r_{12} = |\mathbf{r}_2 - \mathbf{r}_1|$. Coulomb systems have simple scaling properties: Energies are proportional to $e^4 m/\hbar^2 \simeq 27.211$ eV and distances to $\hbar^2/(me^2)$. We shall give all results in natural units, which correspond to treating Eq. (1) as if $m/\hbar^2 = e^2 = 1$. The orbital wavefunction should be antisymmetric for a spin triplet and symmetric for the ground-state spin singlet, which we shall consider first.

### A. The helium atom and the heavier ions

The case of $Z \geq 2$ is treated in most textbooks, and we give only a brief review for the sake of completeness. If the last term of Eq. (1) is omitted, the Hamiltonian is exactly solvable. The unperturbed energy of the ground state is $E_0 = -Z^2$, and the wavefunction is $\Psi(Z) = (Z^3/\pi)\exp[-Z(r_1+r_2)]$. To first order in the repulsion $r_{12}^{-1}$, the energy is approximated and upper bounded by $E_0 + E_1 = -Z^2 + \langle \Psi_Z | r_{12}^{-1} | \Psi_Z \rangle$ ($E_0 + E_1$ is the variational energy corresponding to the trial wavefunction $\Psi_Z$).

The matrix element $\langle \Psi(Z) | r_{12}^{-1} | \Psi(Z) \rangle$ is routinely estimated by a partial-wave expansion. It is sufficient, as done, for example, by Peebles,[14] to use Gauss's theorem, which states that the potential created at distance $r_2$ by a spherical shell $\delta q_1$ of radius $r_1$ is $\delta q_1/r_2$ if $r_1 < r_2$ and $\delta q_1/r_1$ if $r_1 > r_2$ to give

$$E_1 = 4Z^6 \int_0^\infty \exp(-2Zr) r^2 dr \left[ \int_0^r \frac{\exp(-2Zr')}{r} r'^2 dr' \right.$$
$$\left. + \int_r^\infty \frac{\exp(-2Zr')}{r'} r'^2 dr' \right] = \frac{5Z}{8}. \tag{2}$$

For $Z=2$ we obtain the energy of $-2.75$, in comparison to $E = -2.903\,72\ldots$ from the most sophisticated estimates[15,16] and the lowest dissociation threshold $E_{th} = -2$. In this approach the energy to bind two electrons must be less than the ground-state energy of one electron atom, which in our units is $Z^2/2$. Thus, $-Z^2 + 5Z/8 < -Z^2/2$, or $Z > 5/4$. An easy and instructive improvement consists of replacing $\Psi(Z)$ by

$$\Psi(\alpha) = (\alpha^3/\pi)\exp[-\alpha(r_1 + r_2)], \tag{3}$$

where $\alpha$ is a variational parameter that is a measure of the effective charge seen by each electron. The matrix elements are the same as for $\alpha = Z$, and the variational energy, denoted $E[\Psi]$, is

$$E[\Psi] = \min_\alpha \left[ \alpha^2 - 2Z\alpha + \frac{5\alpha}{8} \right] = -\left( Z - \frac{5}{16} \right)^2. \tag{4}$$

The minimum is reached for $\alpha = Z - 5/16$. For $Z=2$, Eq. (4) gives the improved result $\tilde{E} \simeq -2.8477$. Binding with this wavefunction is demonstrated only for $Z \gtrsim 1.067$. Thus $Z = 1$ requires another treatment, as discussed in Sec. II B.

### B. The negative hydrogen ion

Variational wavefunctions that bind H$^-$ have been given by Bethe, Hylleraas, and others.[2] For instance, the correlation factor $(1 + \beta r_{12})$ or $\exp(\gamma r_{12})$ can be inserted into wavefunction (3). The most elegant solution is perhaps that of Chandrasekhar,[13,9] which is (un-normalized),

$$\Phi = \exp(-ar_1 - br_2) + \epsilon \exp(-br_1 - ar_2), \quad (\epsilon = +1), \tag{5}$$

where the permutation symmetry is explicitly broken by $a \neq b$ and restored by the second term. In comparison to the standard shell-model wavefunction in Eq. (3), sometimes labeled $(1s)^2$, this wavefunction is named "unrestricted" by Goddard,[17] who gives a generalization.

The matrix elements of $\Phi$ involve the same integrals as the simpler wavefunction $\Psi_\alpha$, and it is straightforward to derive the kinetic energy $T$, the potential $V$, and the normalization $N$ entering the expectation value $\bar{E}(a,b) = \langle \Phi | H | \Phi \rangle$ of the Hamiltonian

$$\bar{E}(a,b) = \frac{\langle \Phi | H | \Phi \rangle}{\langle \Phi | \Phi \rangle} = \frac{T+V}{N}, \tag{6}$$

$$N = \frac{1}{8a^3 b^3} + \frac{8\epsilon}{(a+b)^6}, \tag{7}$$

$$T = \frac{1}{16ab^3} + \frac{1}{16a^3 b} + \frac{8ab\epsilon}{(a+b)^6}, \tag{8}$$

$$V = -\frac{Z}{8a^2 b^3} - \frac{Z}{8a^3 b^2} - \frac{8Z\epsilon}{(a+b)^5} + \frac{5\epsilon}{2(a+b)^5}$$
$$+ \frac{a^2 + 3ab + b^2}{8a^2 b^2 (a+b)^3}, \tag{9}$$

where the attractive terms (proportional to $Z$) are supplemented by the contribution from $1/r_{12}$. The variational energy is $E[\Phi] = \min_{a,b} \bar{E}(a,b)$.

Because H$^-$ is weakly bound, the interpretation is that of one electron far away and the other one near the nucleus, feeling an almost unscreened Coulomb potential. This picture suggests the following approximation: We freeze $a = Z = 1$ and assume that one of the electrons is unperturbed; we then vary $b$ to obtain a first minimum $\bar{E}(1, b_0) \simeq -0.5126$, which already establishes binding. This minimum is reached for $b_0 \simeq 0.279$ (see the dashed curve in Fig. 1).

The use of standard minimization software easily leads to the best minimum $E[\Phi] \simeq -0.5133$ for $a \simeq 1.039$ (very close to the approximate $a=1$) and $b \simeq 0.283$ (or $a \leftrightarrow b$). For comparison, the best energy for an infinitely massive proton
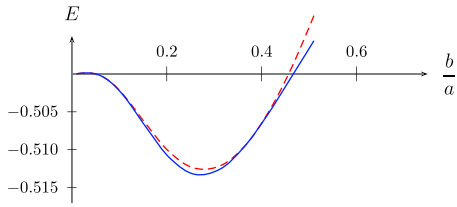
Fig. 1. One parameter minimization of the variational energy $\bar{E}(a,b)$ of H$^-$ obtained from the Chandrasekhar wavefunction with the approximation of a fixed $a=1$ (dashed curve) and without approximation but using the virial theorem, which removes one parameter (solid curve).
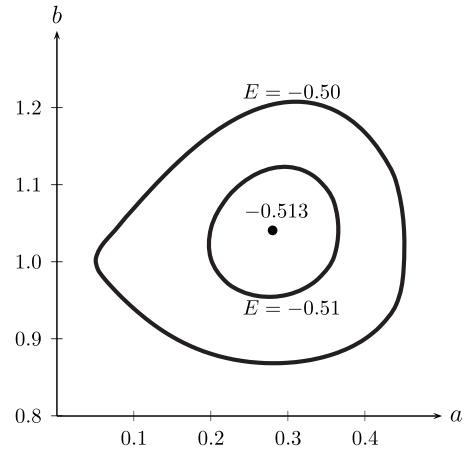


Fig. 2. Contour plot of the variational energy $\bar{E}(a,b)$, given by Eq. (6), of Chandrasekhar wavefunction (5). The symmetric part where $a<b$ is not shown.

is[15,18] $E \approx -0.52775$. As seen in Fig. 2, the minimum is not extremely sharp; however, the stability criterion $\bar{E}(a,b) < 0.5$ clearly requires $b \ll a$ (or $a \ll b$).

The task of minimizing $\bar{E}(a,b)$ or any similar variational energy can be simplified by using the virial theorem, which also holds for the best variational solution, with the mild restriction that the set of trial functions be globally invariant under rescaling.[19,20] Also see Refs. 21–23. A simple derivation of the virial theorem is based on the property that the expectation value of the Hamiltonian remains stationary near an eigenvector. In particular, if one considers the scaling $\Psi(\boldsymbol{r}_1,\ldots) \to \lambda^{-3n/2}\Psi(\lambda\boldsymbol{r}_1,\ldots)$, where $n$ is the number of internal variables and the factor $\lambda^{-3n/2}$ maintains normalization, the expectation value should remain stationary near $\lambda=1$. For the Coulomb problem this requirement means that $\lambda^2 T + V/\lambda$ is minimal at $\lambda=1$, that is, $V=-2T$. This derivation works for both the exact solution and the best variational approximation. For instance, for the Chandrasekhar wavefunction, we can set $a=a_0(1+x)$ and $b=a_0(1-x)$. For a given value of $x$, the minimization over the overall scale $a_0$ fixes the proper balance of the kinetic and potential energy, as required by the virial theorem. We are left with minimizing $-V^2/4NT$ over the single variable $x$ or over $b/a$ to recover the minimum at $E \approx -0.5133$, as shown in Fig. 1 (solid curve).

## C. Varying the proton charge

The method used for H$^-$ can be applied to other values of $Z$. For $Z \geq 2$ wavefunction (5) gives an energy $E[\Phi]=$

$-2.8757$ instead of $E[\Psi] \approx -2.8477$ from factorized wavefunction (3). As $Z$ increases, the improvement becomes less significant, that is, factorized wavefunction (3) works almost equally well (see Tables I and II).

Alternatively, we can investigate how far we can decrease $Z$ without losing the bound state. It can be checked that stability remains down to $Z \approx 0.949$ with wavefunction (5). The most sophisticated estimate[24–26] of the critical charge to bind two electrons is $Z_c \approx 0.9107$, which comes from the $1/Z$ expansion. The Hamiltonian is rewritten as

$$\frac{H}{Z^2} = \frac{\boldsymbol{p}_1^2}{2m} + \frac{\boldsymbol{p}_2^2}{2m} - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{Zr_{12}}, \qquad (10)$$

and the energy is expanded in powers of $1/Z$. From Eq. (2), the first terms are $Z^2[-1+5/(8Z)+\ldots]$. Elaborate studies[24–26] beyond the scope of this article have shown that the first few terms in the expansion are

Table I. Binding energies (in natural units) for a series of central charge $Z$ and electron spin $S$. The experimental energy $E_{\text{exp}}$ is taken from current data bases (Refs. 30 and 31) and compared to the best nonrelativistic calculation with an infinitely massive nucleus, $E_{\text{NR}}$ (Refs. 18, 32, and 33), the simplest Hartree–Fock type of calculation with an effective charge, $E_{\text{fac}}$ corresponding to Eq. (3) for $S=0$ and Eqs. (17) for $S=1$, and the energy from the Chandrasekhar wavefunction (5) with $\epsilon=+1$ for $S=0$ and $\epsilon=-1$ for $S=1$, with optimized range parameters $a$ and $b$.

| $Z$ | $S$ | $E_{\text{exp}}$ | $E_{\text{NR}}$ | $E_{\text{fac}}$ | $E_{\text{C}}$ | $a$ | $b$ |
|---|---|---|---|---|---|---|---|
| 1 | 0 | $-0.5274$ | $-0.5277$ | $-0.4727$ | $-0.5133$ | 1.04 | 0.28 |
| 2 | 0 | $-2.9034$ | $-2.9037$ | $-2.8477$ | $-2.8757$ | 2.18 | 1.19 |
| 2 | 1 | $-2.1750$ | $-2.1752$ | $-2.1666$ | $-2.1607$ | 1.97 | 0.32 |
| 3 | 0 | $-7.2800$ | $-7.2799$ | $-7.2227$ | $-7.2488$ | 3.29 | 2.08 |
| 3 | 1 | $-5.1103$ | $-5.1107$ | $-5.1026$ | $-5.0718$ | 2.93 | 0.60 |
| 4 | 0 | $-13.657$ | $-13.656$ | $-13.598$ | $-13.623$ | 4.39 | 2.98 |
| 4 | 1 | $-9.2988$ | $-9.2972$ | $-9.2892$ | $-9.2240$ | 3.89 | 0.88 |
| 8 | 0 | $-59.195$ | $-59.157$ | $-59.098$ | $-59.122$ | 8.68 | 6.69 |
| 8 | 1 | $-38.579$ | $-38.545$ | $-38.537$ | $-38.233$ | 7.73 | 2.00 |

Table II. Binding energies of $H^-$ ($Z=1$) and He ($Z=2$) with an infinitely massive nucleus obtained from the variational wavefunction (18). For He we also show the two first excitations in the scalar sector: $He^*$ (para) with the same spin $S=0$ as the ground state and $He^*$ (ortho) with a symmetric $S=1$ and thus an antisymmetric space wavefunction.

| $N$ | $a_i, b_i, c_i$ | $H^-$ | He | $He^*$ (para) | $He^*$ (ortho) |
|---|---|---|---|---|---|
| 1 | $a=b=Z$, $c=0$ | $-0.375$ | $-2.75$ | | |
| 1 | $a=b$, $c=0$ | $-0.47266$ | $-2.84766$ | | |
| 1 | $a=b$, $c\neq0$ | $-0.50790$ | $-2.88962$ | | |
| 1 | $a\neq b$, $c=0$ | $-0.51330$ | $-2.87566$ | | $-2.16064$ |
| 1 | $a\neq b$, $c\neq0$ | $-0.52387$ | $-2.89953$ | | $-2.16153$ |
| 2 | $a\neq b$, $c\neq0$ | $-0.52496$ | $-2.90185$ | $-2.14461$ | $-2.17512$ |
| 3 | $a\neq b$, $c\neq0$ | $-0.52767$ | $-2.90328$ | $-2.14538$ | $-2.17521$ |
| 4 | $a\neq b$, $c\neq0$ | $-0.52771$ | $-2.90347$ | $-2.14551$ | $-2.17522$ |
| "Exact"[a] | | | $-2.90372$ | $-2.14597$ | $-2.17523$ |

[a]Reference 15.

$$E = -Z^2 \left( 1 - \frac{5}{8Z} + \frac{0.157666429}{Z^2} - \frac{0.008699032}{Z^3} \right.$$
$$\left. + \frac{0.000888707}{Z^4} + \dots \right). \tag{11}$$

The convergence of the series is associated with well isolated bound states lying below the threshold. When the convergence breaks, the binding is lost. The radius of convergence $1/Z \simeq 1.098$ leads to the critical charge $Z_c \simeq 0.9107$.

### D. Proton recoil

We can examine the effect of a finite mass for the proton and more generally study the stability of $(M^\pm, m^\mp, m^\mp)$ as a function of the mass ratio $M/m$. The Hamiltonian now reads

$$H = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + \frac{p_3^2}{2M} - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{r_{12}}. \tag{12}$$

The negative hydrogen ion corresponds to $M/m \to \infty$, the positronium ion, $Ps^-$, corresponds to $M/m=1$, and the molecular-hydrogen ion, $H_2^+$, corresponds to $M/m \to 0$.

Hill[27] showed that Chandrasekhar's wavefunction (5) demonstrates binding for any $M/m$. When $M/m$ is varied, the minimum is reached with the same $b/a$ and the same quality of binding, as measured by the ratio of the best variational energy to the threshold energy. The proof is rather straightforward. We introduce the standard coordinates

$$x = r_1 - r_3, \quad y = r_2 - r_3, \quad R = \frac{mr_1 + mr_2 + Mr_3}{2m + M}, \tag{13}$$

and the conjugate momenta

$$p_x = \frac{(m+M)p_1 - m(p_3+p_2)}{M+2m},$$

$$p_y = \frac{(m+M)p_2 - m(p_3+p_1)}{M+2m}, \tag{14}$$

$$P = p_1 + p_2 + p_3,$$

in terms of which the Hamiltonian becomes

$$H = \frac{P^2}{4m+2M} + \left[ \frac{p_x^2}{2\mu} - \frac{1}{|x|} + \frac{p_y^2}{2\mu} - \frac{1}{|y|} + \frac{1}{|x-y|} \right]$$
$$+ \frac{1}{M} p_x \cdot p_y. \tag{15}$$

Once the center of mass motion is removed, we are left with the Hughes–Eckart term[28] $p_x \cdot p_y / M$ and, in the bracket, a rescaled version of $H^-$ with an infinitely massive proton and two electrons whose mass is $\mu = mM/(m+M)$. The Hamiltonian in the bracket gives stability with respect to decay into a $(M^+, m^-)$ atom and an isolated negative charge. However, the Hughes–Eckart term has zero expectation value using wavefunction (5) with $r_1 \to |x|$ and $r_2 \to |y|$ and in any similar wavefunction in which there is no dependence on the angle between $x$ and $y$. Hence the Chandrasekhar wavefunction gives the same energy as it did for $H^-$, apart from an overall scaling factor $\mu/m$.

### E. Symmetry breaking in three-charge systems

So far we have discussed configurations of the type $(M^+, m^-, m^-)$ with two identical negative particles. We can address the question of stability of more general mass configurations $(M^+, m_1^-, m_2^-)$. The most general case is discussed in Ref. 22 with stable configurations such as $Ps^-$ or $H^-$ and unstable ones such as $(p, \bar{p}, e^-)$. We shall restrict the discussion here to small differences between $m_1$ and $m_2$.

It is known that symmetry breaking lowers the ground state. For instance, one-dimensional systems described by $h = p^2 + x^2 + \lambda x$ have a ground state at $\epsilon = 1 - \lambda^2/4$ shifted down by the odd term $\lambda x$, compared to the even $\lambda = 0$ case. More generally, if $H = H_0 + \lambda H_1$, with $H_0$ even and $H_1$ odd under some symmetry, then the variational principle applied to $H$ with the even ground state $\Psi_0$ of $H_0$ as a trial wavefunction gives for the ground-state $E(\lambda) \leq E(0)$, provided that $\langle \Psi_0 | H_1 | \Psi_0 \rangle = 0$.

Hence, if the $(M^+, m_1^-, m_2^-)$ Hamiltonian is split into[29]

$$H(M^+,m_1^-,m_2^-) = H(M^+,\bar{m}^-,\bar{m}^-) + \frac{m_1^{-1} - m_2^{-1}}{4}(\boldsymbol{p}_1^2 - \boldsymbol{p}_2^2),$$

(16)

where $\bar{m}$ is the average inverse mass and the ground-state energy is shifted down by the second term, that is, $E(M^+,m_1^-,m_2^-) \leq E(M^+,\bar{m}^-,\bar{m}^-)$. But the gain is only second order in $m_1^{-1} - m_2^{-1}$, and the lowest threshold decreases to first order, with $E_2(M,m_2) < E_2(M,\bar{m})$ if $m_1 < m_2$ and thus $\bar{m} < m_2$. Not surprisingly, the net result is that stability deteriorates as the two negative charges are given different masses.

It is an interesting exercise to modify wavefunction (5) and to study the domain of stability of $(M^+,m_1^-,m_2^-)$ as a function of $m_1$ and $m_2$ in the limit $M \to \infty$.

## III. FIRST EXCITATIONS OF TWO-ELECTRON ATOMS AND IONS

### A. Spin-triplet ground state

If wavefunction (5) is used with $\epsilon = -1$, that is, in its antisymmetric version, it becomes a trial wavefunction for the lowest spin-triplet state. For H$^-$ this level is unstable. Some results are shown in Table I for $Z \geq 2$. In particular, we find $E \simeq -2.16064$ for the lowest spin-triplet state of helium, in comparison to $E \simeq -2.17523$ from wavefunctions with many parameters. Also shown in Table I is the result obtained from the simplest alternative wavefunction that comes to mind,

$$\Psi_{a,b}(r_1,r_2) = \frac{\phi_{1s}(a,r_1)\phi_{2s}(b,r_2) - \phi_{2s}(b,r_1)\phi_{1s}(a,r_2)}{\sqrt{2}},$$

(17a)

with

$$\phi_{1s}(a,r) = \frac{a^{3/2}}{\sqrt{\pi}} \exp(-ar),$$

(17b)

$$\phi_{2s}(a,r) = \frac{a^{3/2}}{\sqrt{8\pi}}(1 - ar/2)\exp(-ar/2).$$

For $a=b$ Eqs. (17) represent a standard normalized shell-model wavefunction and corresponds to the fifth column of Table I. The results are slightly better than those from the Chandrasekhar wavefunction. If this wavefunction is used with different range parameters $a$ and $b$ (and thus with nonorthogonal individual wavefunctions), corresponding to a unrestricted Hartree–Fock wavefunction in the notation in Ref. 17, we find slightly better results, especially for small $Z$. For large $Z$, wavefunctions (17), with $a \to b \to Z$, become exact.

### B. Toward a more accurate calculation

For both the spin-singlet and the spin-triplet cases, the Chandrasekhar wavefunction cannot describe completely three-body ground states such as H$^-$. It can be improved by superposing more terms of the same kind. For instance, Goddard[17] considered a symmetrized combination of products of $1s, 2s, \ldots, 5s$ orbitals with different range parameters. For the ground state with spin singlet, he found $E \simeq -0.5138$, which is a modest improvement compared to Chandrasekhar's result $E \simeq -0.5133$, which corresponds to considering only two $1s$ orbitals.

The most general scalar wavefunction depends on three variables, which can be chosen as the relative distances $r_1 = r_{31} = y$, $r_2 = r_{23} = x$, and $r_{12} = z$. Hence the wavefunctions without an explicit $r_{12}$ dependence will never approach the exact solution with arbitrary accuracy.

Starting from Eq. (5), a natural extension is

$$\Psi = \exp(-ax - by - cz) \pm \{a \leftrightarrow b\}$$

(18)

and a superposition of such terms. With a single term ($N = 1$), we obtain the results listed in Table II. Also shown are the improvements brought by superposing $N=2$, 3, and 4 such terms. For larger $N$, the numerical minimization becomes delicate and requires clever tools, such as a stochastic search of the parameters. Frolov,[34] Korobov,[16] and others developed a systematic expansion based on such exponential terms and obtained extremely accurate results.

### C. Hydrogen ion with unnatural parity

Another challenging problem deals with states of unnatural parity $P=(-1)^{L+1}$ if $L$ is the total orbital momentum, in particular the lowest state $L^P=1^+$. Consider again the $(p,e^-,e^-)$ system, although similar considerations can be developed in the four-body case. If we neglect the spins and intrinsic parities, the ground state has angular momentum and parity $L^P=0^+$. It is the only level of H$^-$ below the lowest threshold H$(1s)+e^-$, as shown by Hill.[27]

However, the state with quantum numbers $L^P=1^+$, that is, unnatural parity, cannot decay into H$(1s)+e^-$, at least as long as radiative corrections and spin-dependent effects are neglected. Its lowest threshold is H$(2p)+e^-$ at $E_{th}=-0.125$. It has been discovered[35] that the lowest state of H$^-$ with $1^+$ lies below this threshold, and other calculations[36–38] have confirmed the energy $E \simeq -0.1253$. The problem is to find the most economical way of demonstrating this binding.

The simplest wavefunction bearing the right quantum numbers for this state is

$$\Psi(a,b,c) = (\boldsymbol{x} \times \boldsymbol{y})_i[\exp(-ax - by - cz) + \{a \leftrightarrow b\}],$$

(19)

where $i$ is any projection of the vector product.

After angular integration, we are left with integrating a polynomial in $x$, $y$, and $z$ times an exponential; the result can be deduced from a single generating function, as outlined in the Appendix. After optimization of the range parameters $a$, $b$, and $c$ (or two of them if we use the virial theorem), we can show that this wavefunction just fails to bind the unnatural parity state of H$^-$. We need a superposition such as

$$\sum_i \alpha_i \Psi(a_i,b_i,c_i).$$

(20)

For a given set of range parameters $\{a_i,b_i,c_i\}$, the coefficients $\alpha_i$ and the resulting energy are given by a generalized eigenvalue problem. Then the range parameters can be adjusted by standard techniques if the number of terms is limited. If this number increases, special care is required to avoid numerical instabilities. To simplify the minimization, we can extract the range parameters $a_i$, $b_i$, and $c_i$ from an arithmetic series $\alpha, \alpha+\beta, \alpha+2\beta, \ldots$, allowing the possibility of equal values, for example, $b_i=c_i$. The minimization thus runs only on $\alpha$ and $\beta$. If $\alpha < 0$ and $\beta > 0$, which help in introducing some anticorrelation among the two electrons,

we should impose $a_i + b_i > 0$, $b_i + c_i > 0$, and $c_i + a_i > 0$. For H⁻ with $1^+$ we demonstrated the stability with a few terms and thus confirmed earlier results.[35–38]

If we do the calculation for Ps⁻, we never reach a variational energy below the Ps($2p$)+$e^-$ threshold. This result confirms the conclusion by Mills, who found that this state is unbound.[39]

## IV. TWO-ELECTRON MOLECULES

### A. The positronium molecule

In 1945 Wheeler suggested a variety of new states containing positrons, which could be stable in the limit that internal annihilation ($e^+ + e^- \to \gamma$'s) is neglected.[11] Among the predictions was the existence of the positronium molecule, Ps$_2$ ($e^+, e^+, e^-, e^-$). In 1946 Ore tried to do the calculations for this molecule and concluded that it is likely to be unstable.[40] The next year, Hylleraas and Ore[41] presented a beautiful proof of stability based on the wavefunction

$$\Psi = \exp(-ar_{13} - br_{14} - ar_{24} - br_{23}) + \{a \leftrightarrow b\}, \quad (21)$$

which is an obvious generalization of Eq. (5). All the matrix elements can be calculated analytically.[22,41] Some hints are given in the Appendix. With $a + b = 1$ and $a - b = \beta$, the normalization, kinetic energy, and potential energy are

$$N = \frac{33}{16} + \frac{33 - 22\beta^2 + 5\beta^4}{16(1 - \beta^2)^3}, \quad (22a)$$

$$T = \frac{21}{8} - \frac{3\beta^2}{2} + \frac{21 - 6\beta^2 + \beta^4}{8(1 - \beta^2)^3}, \quad (22b)$$

$$V = \frac{19}{6} + \frac{21 - 18\beta^2 + 5\beta^4}{4(1 - \beta^2)^3} - \frac{1}{(1 - \beta^2)^2}$$
$$\times \left[ 1 - \frac{5\beta^2}{8} - \frac{1}{4\beta^4} + \frac{7}{8\beta^2} + \frac{(1 - \beta^2)^4}{4\beta^6} \ln\frac{1}{1 - \beta^2} \right]. \quad (22c)$$

By using the virial theorem, the quantity $E = -V^2/(4TN)$ is minimized by varying $\beta$. Although it does not include an explicit dependence on $r_{12}$ or $r_{34}$, wavefunction (21) suffices to establish binding at $E \simeq -0.5042$, below the threshold for spontaneous dissociation into two positronium atoms, at $E_{th} = -0.5$. This energy has been lowered by more and more sophisticated computations[42] to $\approx -0.51600$. It was later realized that there are excited states whose threshold is higher than two positronium atoms in the ground state due to selection rules (see, for example, Ref. 43). Indirect experimental evidence for the Ps$_2$ molecule was reported recently,[12] 62 years after its prediction.

### B. Other molecules

Once the positronium molecule is shown to be stable, we may study what happens for other mass configurations. Although the hydrogen molecule ($M^+, M^+, m^-, m^-$) is better described from the large $M/m$ limit, that is, the Born–Oppenheimer approximation, it is amazing that its stability can be understood from the $M = m$ limit. It is also instructive to study whether or not symmetry breaking improves binding.

The molecule ($\mu^+, \mu^-, \mu^-, \mu^-$), that is, any rescaled version of Ps$_2$, has many symmetries: Exchange of the positive or the negative particles and overall charge conjugation. For simplicity, consider a breaking of permutation symmetry, identically in the positive and the negative sectors, keeping the average inverse mass $\mu^{-1}$ constant. This symmetry breaking corresponds to writing the Hamiltonian as[22]

$$H(M^+, m^+, M^-, m^-) = H(\mu^+, \mu^+, \mu^-, \mu^-) + \frac{M^{-1} - m^{-1}}{4}$$
$$\times (p_1^2 - p_2^2 + p_3^2 - p_4^2). \quad (23)$$

The second term decreases the energy of the molecule. The same effect is observed as for the three-body ion: The energy of the molecule decreases less substantially than the energy of the atom-atom threshold, which benefits from the property of two-body energies,

$$E_2(M^+, M^-) + E_2(m^+, m^-) \le 2E_2(\mu^+, \mu^-). \quad (24)$$

Detailed numerical studies have shown that stability is lost for $M/m \gtrsim 2.2$ (or $m/M \gtrsim 2.2$).[44]

If charge conjugation is broken instead, that is, if the mass configuration becomes ($M^+, M^+, m^-, m^-$), the decomposition is

$$H(M^+, M^+, m^-, m^-) = H(\mu^+, \mu^+, \mu^-, \mu^-) + \frac{M^{-1} - m^{-1}}{4}$$
$$\times (p_1^2 + p_2^2 - p_3^2 - p_4^2), \quad (25)$$

and again the four-body ground-state energy is lowered by the second term. Now, the threshold remains constant at $2E_2(M^+, m^-) = 2E_2(\mu^+, \mu^-)$, and thus the stability is improved. The hydrogen molecule is bound by about 17% below the atom-atom threshold, compared to only about 3% for the positronium molecule.

## V. SUMMARY

We have reviewed how the stability of the ground state of H⁻ and the lowest spin-triplet state of helium can be reached with simple wavefunctions whose matrix elements can be determined by straightforward calculus. A more delicate and less advertised problem is that of the stability of the unnatural parity states, which forces us to push the variational expansion further to demonstrate binding.

The main message is that the Hartree–Fock method, that is, factorized wavefunctions with suitable (anti)symmetrization, is very efficient for deeply bound systems but fails in demonstrating the binding of states at the edge between stability and spontaneous dissociation. This failure is also observed in nuclear physics: Halo nuclei with a weakly bound external neutron and the Borromean nuclei with two external neutrons require special treatment.

The strategy initiated by Hylleraas,[45] Chandrasekhar,[13] and others consists of using a basis of functions for which each term breaks permutation symmetry. The proper boson or fermion statistics is restored by superposing terms deduced by permutation. The same strategy guided Hylleraas and Ore[41] when they derived the first proof of stability of the positronium molecule, and it also forms the foundation for the most recent calculations of this molecule. For example, in their study of the positronium molecule,[42] Suzuki and Varga[46] used a basis of correlated Gaussians and their own variant of the parameter search. This method is becoming

widely used in quantum chemistry and other few-body problems. It consists of describing the wavefunctions as superpositions of states such as

$$\psi = \exp\left[-\sum_{i<j} a_{ij}\boldsymbol{x}_i \cdot \boldsymbol{x}_j\right] + \ldots, \tag{26}$$

where $\boldsymbol{x}_1, \ldots, \boldsymbol{x}_n$ are the internal variables and the ellipses are meant for terms deduced by permutation, charge conjugation, and any other relevant symmetry, which can be explicitly enforced.

## APPENDIX: CALCULATION OF THE MATRIX ELEMENTS

We give here some suggestions on how to determine the matrix elements, which for the wavefunctions in Eqs. (3) and (5) have been given explicitly. Consider the generalization $\phi = \exp(-ax - by - cz) \equiv |a,b,c\rangle$, whose symmetrized or antisymmetrized version, Eq. (18), is used for spin-singlet and spin-triplet states, respectively. Here $\boldsymbol{x} = \boldsymbol{r}_2 - \boldsymbol{r}_3$, $x = |\boldsymbol{x}|$, etc. The matrix elements are integrals over $xyz\,\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z$, restricted by the triangular inequality, and can be deduced from the generic function

$$F_3(\alpha,\beta,\gamma) = \int\int\int_{|x-y|\le z\le x+y}$$
$$\times \exp(-\alpha x - \beta y - \gamma z)\,\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z$$
$$= \frac{4}{(\alpha+\beta)(\beta+\gamma)(\gamma+\alpha)}, \tag{A1}$$

and its derivatives

$$G(i,j,k;\alpha,\beta,\gamma) = (-1)^{i+j+k}\frac{\partial^{i+j+k}F_3(\alpha,\beta,\gamma)}{\partial\alpha^i\,\partial\beta^j\,\partial\gamma^k}. \tag{A2}$$

For instance, the normalization of Eq. (5), besides a factor $8\pi^2$ due to trivial angular integration, is

$$\langle a,b,c|a,b,c\rangle = G(1,1,1,2a,2b,2c). \tag{A3}$$

A potential energy term is similar, for example,

$$\langle a,b,c|r_{12}^{-1}|a,b,c\rangle = G(1,1,0,2a,2b,2c). \tag{A4}$$

The calculation is easily extended to nondiagonal terms, with $2a \to a+a'$ etc.

Consider now the term $\boldsymbol{p}_1$ of the kinetic energy. It is a linear combination of gradients with respect to the distances,

$$\boldsymbol{p}_1 = (-i)[\boldsymbol{\nabla}_z - \boldsymbol{\nabla}_x]. \tag{A5}$$

Including additional constant factors and $\hat{\boldsymbol{y}} \cdot \hat{\boldsymbol{z}} = (x^2 - y^2 - z^2)/(2yz)$ gives

$$\langle a,b,c|\boldsymbol{p}_1^2|a,b,c\rangle = (bb' + cc')\langle a,b,c|a,b,c\rangle$$
$$-\frac{bb' + cc'}{2}[G(3,0,0,\bar{a},\bar{b},\bar{c})$$
$$-G(1,2,0,\bar{a},\bar{b},\bar{c}) - G(1,0,2,\bar{a},\bar{b},\bar{c})], \tag{A6}$$

where $2\bar{a} = a + a'$ etc. For wavefunction (19) some angular integrals should be done beforehand, and we are left with similar integrals over $x$, $y$, and $z$.

We now consider the four-body problem, with a wavefunction of the type

$$\Psi = \exp(-ar_{13} - br_{14} - cr_{23} - dr_{24}). \tag{A7}$$

If $\boldsymbol{r}_{12}$, $\boldsymbol{r}_{13}$, and $\boldsymbol{r}_{23}$ are chosen as the internal coordinates for a scalar wavefunction and a scalar operator that do not depend explicitly on $r_{34}$, we can work independently with the triplets $(1,2,3)$ and $(1,2,4)$ as done for the three-body systems. After summing over the trivial angular variables, the integrals run over

$$\mathrm{d}\tau = r_{13}r_{14}r_{23}r_{24}\mathrm{d}r_{12}\mathrm{d}r_{13}\mathrm{d}r_{14}\mathrm{d}r_{23}\mathrm{d}r_{24}. \tag{A8}$$

A basic integral is

$$F_4(a,b,c,d,u) = \int \frac{\mathrm{d}r_{12}\mathrm{d}r_{13}\mathrm{d}r_{14}\mathrm{d}r_{23}\mathrm{d}r_{24}}{r_{12}}$$
$$\times \exp(-ar_{13} - br_{23} - cr_{14} - dr_{24} - ur_{12})$$
$$= \frac{16}{(a-b)(a+b)(c-d)(c+d)}$$
$$\times \log\left[\frac{(b+c+u)(a+d+u)}{(a+c+u)(b+d+u)}\right], \tag{A9}$$

where the triangular inequalities are more easily accounted for by using the variables $s_i = r_{1i} + r_{2i}$ and $t_i = r_{1i} - r_{2i}$ for $i = 3,4$. All matrix elements are related to $F$ and its derivatives. For instance, the normalization, first attractive term, and internuclear and electronic repulsion of Eq. (A7) are

$$n(a,b,c,d) = -\left.\frac{\partial F_4(a,b,c,d,u)}{\partial u\,\partial a\,\partial b\,\partial c\,\partial d}\right|_{u=0},$$

$$v_{13}(a,b,c,d) = \left.\frac{\partial^4 F_4(a,b,c,d,u)}{\partial u\,\partial b\,\partial c\,\partial d}\right|_{u=0},$$

$$v_{12}(a,b,c,d) = \frac{\partial^4 F_4(a,b,c,d,0)}{\partial a\,\partial b\,\partial c\,\partial d},$$
$$\tag{A10}$$

$$v_{34}(a,b,c,d) = v_{12}(a,c,b,d).$$

For the kinetic energy of the third particle, for example, we obtain

$$\langle\Psi|\boldsymbol{p}_3^2|\Psi\rangle = (a^2 + b^2)\langle\varphi|\Psi\rangle$$
$$-2ab\langle\varphi|(r_{12}^2 - r_{13}^2 - r_{23}^2)/(2r_{13}r_{23})|\Psi\rangle, \tag{A11}$$

which can be expressed as a combination of derivatives of $F_4$. For nondiagonal matrix elements between the wavefunction in Eq. (A7) and an analogous function with range parameters $a', \ldots, d'$, the coefficients in Eq. (A10) become $aa' + bb'$ and $ab' + a'b$, respectively, and the arguments of $F_4$ are taken to be $(a+a')/2, \ldots, (d+d')/2$.

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