

## Neutral “parent” states of the ionic $\text{He}_2^-$ $^4\Phi_g$

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$\text{He}_2$  is examined in the second state of the  $^3\Pi_g$  symmetry. This state is shown to be one of the two “parent” states of the lowest known stable negative ionic  $\text{He}_2^-$  state of the  $^4\Phi_g$  symmetry. It is compared with the other parent neutral  $\text{He}_2$  state, which is the lowest of the  $^3\Delta_u$  symmetry, with a consequence that the negative ionic state be a closed channel resonance with respect to both of its neutral parent states. Furthermore the third  $\text{He}_2$   $^3\Pi_g$  and the second  $\text{He}_2$   $^3\Delta_u$  states are shown to be the parents of the second  $\text{He}_2^-$   $^4\Phi_g$  resonance.

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### I. INTRODUCTION

Following the discovery of the metastable negative ion  $\text{He}_2^-$  by Bae, Coggiola, and Peterson in 1983 [1], its theoretical identification by Michels [2] as  $^4\Pi_g$  ( $1\sigma_g^2 1\sigma_u 2\sigma_g 1\pi_u$ ), and the analysis of its autodetachment spectrum to  $\text{He}_2$   $\alpha^3\Sigma_u^+$  and to  $\text{He}_2$   $X^1\Sigma_g^+$  [3–6], Adamowicz and Pluta [7,8] have investigated the possibility of the formation of other  $\text{He}_2^-$  metastable states. These are based on two-electron attachment to two possible cores ( $1\sigma_g^2 1\sigma_u$ ), [7] and ( $1\sigma_g^2 2\sigma_g$ ) [8]. All  $\text{He}_2^-$  ionic states calculated in Refs. [7,8] obey the simple underlying physics that the outer electrons are comparably far from the molecular center; this seems to be a necessary condition for the formation of a negative ionic molecule because otherwise the electron closer to the nuclei would be attracted even more, and would screen out the outer electron, leaving it free to detach.

If this is true, one should expect the outer orbitals of both neutral parent states to be comparably diffuse before the formation the negative resonance, and to suffer no substantial deformation after forming the resonance. The stability of these negative ionic states with respect to their neutral parent states has also been examined in Refs. [7] and [8], but the above expectation, strangely enough, seems not always to be fulfilled. It will be clear from this work that this unexpected feature is largely due to an erroneous interpretation of the results obtained by the numerical Hartree-Fock method (NHF) [9,10], because the method does not provide any simple way of node counting, or checking a converged result.

Generally the negative ionic states of Refs. [7] and [8] may be separated in two classes: Those with equilibrium internuclear distance  $R_0 = 2$  a.u., emerging from the core ( $1\sigma_g^2 1\sigma_u$ ), [7] which results to  $\text{He}_2^-$   $^4\Pi_g$ ,  $^4\Phi_g$ , and  $^4I_g$  negative ionic states [7], and those with  $R_0 = 1.2$  a.u. emerging from the core ( $1\sigma_g^2 2\sigma_g$ ), [8] which results to  $\text{He}_2^-$   $^4\Pi_u$ ,  $^4\Phi_u$ , and  $^4I_u$  negative ionic states [8].

The present work concentrates on the first class, in particular on the formation of  $^4\Phi_g$ . The essence of the paper is the following: Given that the outer two electrons of the ionic  $\text{He}_2^-$   $^4\Phi_g$  state resonate at about 17 bohr from the molecular center [7], (it is shown that) the extent of the outer orbital in each of the two neutral parents is not about 5 and 23 bohr

as claimed in Ref. [7], but rather about 12 and 13 bohr. The neutral state of Ref. [7] with the 23-bohr outer orbital is one of the parents of another similar negative ionic  $^4\Phi_g$  resonance, which has the outer two electrons at about  $3\frac{1}{2}$  bohr. The two negative ions have almost the same energy with their parents, differing by only 0.002–0.005 a.u. (they are not substantially different, by +0.030 and –0.070 a.u., as claimed in Ref. [7]), and both are closed channel resonances below their parents (instead of open as claimed in Ref. [7] for the first one). The other neutral state of Ref. [7], with the 5-bohr outer orbital, does not seem to be a parent of any  $^4\Phi_g$  negative ionic state.

Hence this paper has the following framework: (i) The unexpected feature of the substantial deformation of the (outer) electron orbitals forming the negative ion is identified in the calculation of Ref. [7]. (ii) The issue of (i) is resolved by calculating the correct neutral parents of  $^4\Phi_g$  as necessary, with the NHF method [9,10], thus reassessing the question of the boundedness of  $^4\Phi_g$  with respect to its neutral parent states. (iii) The results of (ii) are verified by introducing another method of calculation, based on variational global minimization of the energy of a configuration interaction (CI) using one-electron diatomic molecular orbitals (DMO's). (iv) One further  $^4\Phi_g$  negative ionic state and its neutral parents are discovered via this method. (v) The question of the existence of the  $^4\Phi_g$  negative ionic state as labeled in Ref. [7] is addressed.

In Sec. II all relevant definitions and descriptions are presented; then the present work is analyzed: Sec. III shows the correct identification of the orbitals in  $^4\Phi_g$  of Ref. [7], and in the remaining sections the calculation and the results are exposed.

### II. DEFINITIONS AND DESCRIPTIONS

In order to avoid ambiguities, all states in this section will be identified by three quantities in brackets (label, energy, extent): i.e., their symmetry label, their equilibrium energy  $E_0 = E(R_0)$ , and the root-mean-square (RMS) distance(s) of the outer electron(s) from the molecular center at  $R_0$  (in a.u.). Thus the states considered in this work are as follows:

$$\begin{aligned} \text{He}_2 \ 1^3\Pi_g &: [(1\sigma_g^2 1\sigma_u 1\pi_u), -5.05, 5]; \\ \text{He}_2 \ 2^3\Pi_g &: [(1\sigma_g^2 1\sigma_u 2\pi_u), -4.98, 13]; \\ \text{He}_2 \ 1^3\Delta_u &: [(1\sigma_g^2 1\sigma_u 1\delta_g), -4.98, 12]; \\ \text{He}_2^- \ 1^4\Phi_g &: [(1\sigma_g^2 1\sigma_u 2\pi_u 1\delta_g), -4.98, (16, 19)]; \end{aligned}$$

$$\text{He}_2 \ 3^3\Pi_g : [(1\sigma_g^2 1\sigma_u 3\pi_u), -4.95, 24];$$

$$\text{He}_2 \ 2^3\Delta_u : [(1\sigma_g^2 1\sigma_u 2\delta_g), -4.95, 23];$$

and

$$\text{He}_2^- \ 2^4\Phi_g : [(1\sigma_g^2 1\sigma_u 3\pi_u 2\delta_g), -4.95, (32,33)].$$

(a) *Identification of the unexpected feature in Ref. [7].* Adamowicz and Pluta in Ref. [7] have calculated the negative ionic state  $\text{He}_2^- \ 1^4\Phi_g : [(1\sigma_g^2 1\sigma_u 2\pi_u 1\delta_g), -4.98, (16,19)]$ , which they labeled as  $(1\sigma_g^2 1\sigma_u 1\pi_u 1\delta_g)$ . Furthermore, in an attempt to identify its neutral parents, they also calculated two neutral  $\text{He}_2$  states,  $1^3\Pi_g : [(1\sigma_g^2 1\sigma_u 1\pi_u), -5.05, 5]$  and  $2^3\Delta_u : [(1\sigma_g^2 1\sigma_u 2\delta_g), -4.95, 23]$ , which they labeled in Ref. [7] as  $^3\Pi_g : (1\sigma_g^2 1\sigma_u 1\pi_u)$  and  $^3\Delta_u : (1\sigma_g^2 1\sigma_u 1\delta_g)$  and which they considered as its neutral parents. Thus they conclude that the negative ion in this state is bound with respect to one of its parents and unbound with respect to the other one. Their calculations were performed via the NHF method [9,10] in a single-configuration approximation. However, these states exhibit the following unexpected features [7]: the RMS distance from the diatomic center,  $\langle R^2 \rangle^{1/2}$ , for the  $1\pi_u$  orbital in the  $\text{He}_2 \ 3^3\Pi_g$  state is about 5 a.u. whereas in the  $\text{He}_2^- \ 1^4\Phi_g$  state it is about 16 a.u. Correspondingly, the RMS extent for the  $1\delta_g$  orbital in the  $\text{He}_2 \ 3^3\Delta_u$  state is about 23 a.u., whereas in the  $\text{He}_2^- \ 1^4\Phi_g$  state it is about 19 a.u. The core orbitals in all three states have the same RMS extent, about 1.3 a.u.. In other words, the outer orbitals are reported in Ref. [7] to be substantially deformed in order to form the negative ion.

(b) *Description of the resolution of (a).* The following statements can be made about the above three states of Ref. [7]: (i) The  $\text{He}_2^- \ 1^4\Phi_g : [(1\sigma_g^2 1\sigma_u 2\pi_u 1\delta_g), -4.98, (16,19)]$  state seems to be the lowest state of this symmetry, but it is erroneously identified in Ref. [7]; this is shown in the present work by node counting and by comparing the orbitals of that NHF calculation with corresponding one-electron DMO [11]. (ii) The  $\text{He}_2 \ 2^3\Delta_u : [(1\sigma_g^2 1\sigma_u 2\delta_g), -4.95, 23]$  state is also erroneously identified in Ref. [7]; this has been shown in Ref. [12]. (iii) Finally the  $\text{He}_2 \ 1^3\Pi_g : [(1\sigma_g^2 1\sigma_u 1\pi_u), -5.05, 5]$  state of Ref. [7] is correctly labeled in Ref. [7] and is indeed the lowest state of the  $^3\Pi_g$  symmetry.

Since the neutral states given in Ref. [7]  $\text{He}_2 \ 1^3\Pi_g : [(1\sigma_g^2 1\sigma_u 1\pi_u), -5.05, 5]$ , and  $\text{He}_2 \ 2^3\Delta_u : [(1\sigma_g^2 1\sigma_u 2\delta_g), -4.95, 23]$ , are rather irrelevant to the negative ion,  $\text{He}_2^- \ 1^4\Phi_g : [(1\sigma_g^2 1\sigma_u 2\pi_u 1\delta_g), -4.98, (16,19)]$ , the latter should be compared with its true parents, namely,  $\text{He}_2 \ 2^3\Pi_g : [(1\sigma_g^2 1\sigma_u 2\pi_u), -4.98, 13]$  and  $\text{He}_2 \ 1^3\Delta_u : [(1\sigma_g^2 1\sigma_u 1\delta_g), -4.98, 12]$ , among which one is known in the literature and one is unknown: (i) The latter,  $1^3\Delta_u$ , is known as the lowest state of the  $^3\Delta_u$  symmetry; it has been calculated in Ref. [12]. (ii) However, the other one,  $2^3\Pi_g$ , is the second state of the  $^3\Pi_g$  symmetry, is unknown, and is calculated here.

(c) *The calculations of the present work.* (i) The state  $\text{He}_2 \ 2^3\Pi_g : [(1\sigma_g^2 1\sigma_u 2\pi_u), -4.98, 13]$  is examined here in relation to the other parent,  $\text{He}_2 \ 1^3\Delta_u : [(1\sigma_g^2 1\sigma_u 1\delta_g), -4.98, 12]$  and to their negative daughter,  $\text{He}_2^- \ 1^4\Phi_g : [(1\sigma_g^2 1\sigma_u 2\pi_u 1\delta_g), -4.98, (16,19)]$ —the lowest state of the  $^4\Phi_g$  symmetry, as calculated in Ref. [7].

Thus it is shown here that the *second*  $\text{He}_2 \ 3^3\Pi_g$  state (this work), and the *lowest*  $\text{He}_2 \ 3^3\Delta_u$  state [12] are the parents of the *lowest*  $\text{He}_2^- \ 1^4\Phi_g$  resonance [7]. This result was obtained via the same NHF method [9,10] as in Ref. [7]. It is also verified via a straightforward variational method (global energy minimization) developed here for this purpose (called GRAM below), because the verification with other standard basis-set methods failed (they do not converge).

(ii) Furthermore it will be shown by the variational (GRAM) method that the *third*  $\text{He}_2 \ 3^3\Pi_g : [(1\sigma_g^2 1\sigma_u 3\pi_u), -4.95, 24]$  and the *second*  $\text{He}_2 \ 2^3\Delta_u : [(1\sigma_g^2 1\sigma_u 2\delta_g), -4.95, 23]$  states are the parents of the *second*  $\text{He}_2^- \ 2^4\Phi_g : [(1\sigma_g^2 1\sigma_u 3\pi_u 2\delta_g), -4.95, (32,33)]$  resonance. For this result NHF and other attempted standard basis-set methods failed (did not converge).

### III. ORBITAL IDENTIFICATION

In this section a correct identification of the orbitals of  $\text{He}_2^- \ 1^4\Phi_g : [(1\sigma_g^2 1\sigma_u 2\pi_u 1\delta_g), -4.98, (16,19)]$  [7] is presented.

The state was recalculated here with the same method (NHF) [9,10]. An examination of the NHF orbitals by node counting and by a comparison with appropriate one-electron DMO [11] reveals that the state  $\text{He}_2^- \ 1^4\Phi_g$  of Ref. [7] is actually  $(1\sigma_g^2 1\sigma_u 2\pi_u 1\delta_g)$ . The examination uses the following knowledge:

(i) As recalled [11], the DMO's, if expressed in spheroidal prolate coordinates  $(\xi, \eta, \phi)$  (see Appendix), are separated into the  $\xi$ , the  $\eta$ , and the  $\phi$  parts:  $\Psi_{\text{DMO}}(\xi, \eta, \phi) = \Xi(\xi)H(\eta)e^{im\phi}$ . The DMO's may be labeled by the united-atom-limit quantum numbers (UAQN)  $(nlm)$ ; then the number of nodes of the functions  $\Xi(\xi)$  and  $H(\eta)$  are  $n-l-1$ , and  $l-m$ , respectively [11]. Hence  $1\pi_u$  with UAQN (211) and  $1\delta_g$  with UAQN (322), have no nodes, while  $2\pi_u$  with UAQN (311) has one node.

(ii) As mentioned in Ref. [7], the orbitals involved in the above resonance are separated in two classes: the first two core orbitals  $1\sigma_g$  and  $1\sigma_u$ , which are almost identical to the orbitals of the positive ion  $\text{He}_2^+ \ 2^2\Sigma_u^+ : (1\sigma_g^2 1\sigma_u)$  with an RMS distance  $\langle R^2 \rangle^{1/2}$  from the molecular center of typically 1.3 a.u., and the second two outer and diffuse orbitals  $\pi_u$  and  $\delta_g$  in which the electrons, on the average, are comparably far from the center, with a typical RMS extent of 16–19 a.u. [7]. As will be seen, the outer orbitals of both neutral parent states are comparably diffuse in order to form a negative resonance. Evidently, only the outer orbitals will be considered.

Thus for the ionic state  $\text{He}_2^- \ 1^4\Phi_g$  of Ref. [7], its self-consistent (SCF) outer orbitals  $\pi_u$  and  $\delta_g$  are satisfactorily approximated by corresponding and appropriately screened DMO's. This is intuitively evident and in practice means that the main term  $X_1(\xi)$  of a partial wave expansion [9], expressed in spheroidal prolate coordinates,  $\Psi_{\text{SCF}}(\xi, \eta, \phi) = \sum_{lm} X_1(\xi) Y_{lm}(\eta, \phi)$ , [9] is quite similar to appropriate  $\pi_u$  and  $\delta_g$  DMO's. As seen from Figs. 1 and 2 these orbitals are  $2\pi_u$  and  $1\delta_g$ .

Figure 1 shows the main (the first) term  $X_1(\xi)$  of the outer SCF orbitals  $\pi_u$  and  $\delta_g$  of the above  $\text{He}_2^- \ 1^4\Phi_g$  state recalculated with the same method (NHF) [9,10]. The num-

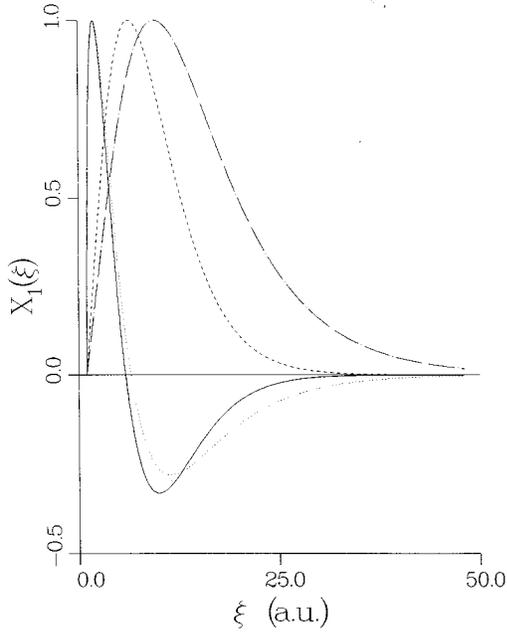


FIG. 1. The self-consistent (SCF)  $2\pi_u$  (dotted line) and  $1\delta_g$  (chain-dotted line) orbitals of the ionic  $\text{He}_2^- \ 4\Phi_g$ :  $(1\sigma_g^2 1\sigma_u 2\pi_u 1\delta_g)$  state [7] compared with the SCF orbitals  $2\pi_u$  (solid line) of the neutral  $\text{He}_2 \ 3\Pi_g$ :  $(1\sigma_g^2 1\sigma_u 2\pi_u)$  state (present work) and  $1\delta_g$  (dashed line) of the neutral  $\text{He}_2 \ 3\Delta_u$ :  $(1\sigma_g^2 1\sigma_u 1\delta_g)$  [12]. The  $2\pi_u$  orbitals have one node and the negative ion orbitals are the more diffuse ones.  $X_1(\xi)$  is the main (the first) term in a partial wave expansion [10] of the SCF orbital wave function expressed in spheroidal prolate coordinates. The internuclear distance is 2 a.u.

ber of nodes are clearly seen as well as the extent of the orbitals. On the other hand Fig. 2 identifies the two  $\pi_u$  SCF orbitals of interest with the DMO's  $2\pi_u$  (the dashed line) and  $1\pi_u$  (the solid line), defined by UAQN (311) and (211), respectively, computed with effective nuclear charges  $z_a^* = z_b^* = 0.4147$  and 0.5 a.u. respectively, at  $R_0 = 2$  a.u. [The value 0.4147 has been determined in single configuration by the variational (GRAM) method and makes it almost identical to the SCF  $2\pi_u$  orbital.]

Thus by comparing with corresponding SCF orbitals of the parent neutral  $\text{He}_2$  states  $3\Pi_g$  (see Fig. 1) and  $3\Delta_u$  (see Ref. [12]) as well as with corresponding pure DMO's (Fig. 2) it is immediately seen that the SCF  $\pi_u$  orbital of the  $\text{He}_2^- \ 4\Phi_g$  state, with one node, may be identified as the  $2\pi_u$ , corresponding to a DMO with UAQN (311), rather than the  $1\pi_u$ , which would correspond to a DMO with UAQN (211), and which would have no nodes, while the SCF  $\delta_g$  orbital is indeed shown to be  $1\delta_g$  (without nodes) as correctly claimed in Ref. [7].

Hence the above negative ionic molecular state is practically the  $\text{He}_2^- \ 4\Phi_g$ :  $(1\sigma_g^2 1\sigma_u 2\pi_u 1\delta_g)$  state. Nevertheless it seems to be the *lowest* ionic  $\text{He}_2^-$  state of the  $4\Phi_g$  symmetry [7], instead of the "reasonably" expected  $(1\sigma_g^2 1\sigma_u 1\pi_u 1\delta_g)$ . In the following the state  $(1\sigma_g^2 1\sigma_u 2\pi_u 1\delta_g)$  will be denoted by  $1^4\Phi_g$ .

The parents of this state, which will determine its stability with respect to neutral  $\text{He}_2$ , will be denoted in the following

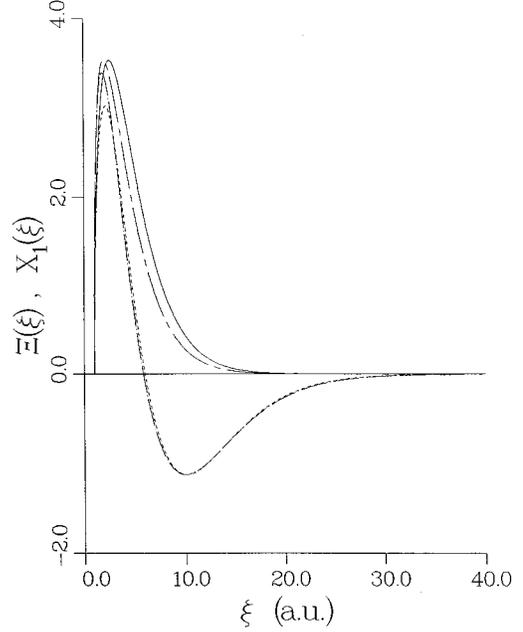


FIG. 2. The SCF orbital  $2\pi_u$  (chain-dotted line) of the second neutral  $\text{He}_2 \ 3\Pi_g$ :  $(1\sigma_g^2 1\sigma_u 2\pi_u)$  state [present work] along with the SCF orbital  $1\pi_u$  (chain-dashed line) of the first neutral  $\text{He}_2 \ 3\Pi_g$ :  $(1\sigma_g^2 1\sigma_u 1\pi_u)$  state [7] compared with corresponding DMO's  $2\pi_u$  (dashed line) and  $1\pi_u$  (solid line), defined by  $(nlm)$  UAQN (311) and (211) respectively. The  $2\pi_u$  orbitals have one node. The terminology is as in Fig. 1.  $\Xi(\xi)$  is the radial-like part of the DMO wave function.

as  $2^3\Pi_g$  ( $1\sigma_g^2 1\sigma_u 2\pi_u$ ), calculated below, and  $1^3\Delta_u$  ( $1\sigma_g^2 1\sigma_u 1\delta_g$ ), known from Ref. [12].

#### IV. CALCULATION AND APPROXIMATIONS

The state  $2^3\Pi_g$ , like  $1^4\Phi_g$  [7] and  $1^3\Delta_u$ , [12] was originally calculated by the program PVMSCCF of McCullough [9] in the NHF approximation using as initial input the following atomic Slater-type orbitals,  $\chi_{nlm}^{\chi}(r, \theta, \phi): \chi_{100}^{1.6}$  for the  $1\sigma_g$  and  $1\sigma_u$  orbitals, and  $a\chi_{211}^{0.3} - b\chi_{311}^{0.1}$ , with  $a = b = 0.71$ , for the  $2\pi_u$  orbital (Fig. 3). [The combinations  $(a, b) = (0.99, 0.14)$  and  $(0.14, 0.99)$  converge to the  $1^3\Pi_g$ , with  $E_0 = -5.05$  a.u., and to  $3^3\Pi_g$ , with  $E_0 = -4.95$  a.u., at  $R = 2$  a.u., respectively]. Because the results (the boundedness of  $1^4\Phi_g$  with respect to  $2^3\Pi_g$ , and  $1^3\Delta_u$ , as discussed later) were contradicting the existing literature [7], an attempt was made to verify them by standard basis-set methods, which failed due to the large diffuseness of the outer orbitals in these excited states. Then a new method was developed for this verification. The new method also enabled the exploration of further aspects of the negative ion formation, i.e., the discovery of the previously unreported in the literature second  $4\Phi_g$  and its neutral parents. This method is a *global* (randomly applied) minimization (GRAM) of a CI total energy within the variational principle, in which all orbitals, expressed as DMO's, are varied simultaneously using their effective nuclear charges  $z_a^*, z_b^*$  as nonlinear variational parameters. (The results from the GRAM method are shown in Figs. 4 and 5.)

Since the original calculation was performed by Mc-

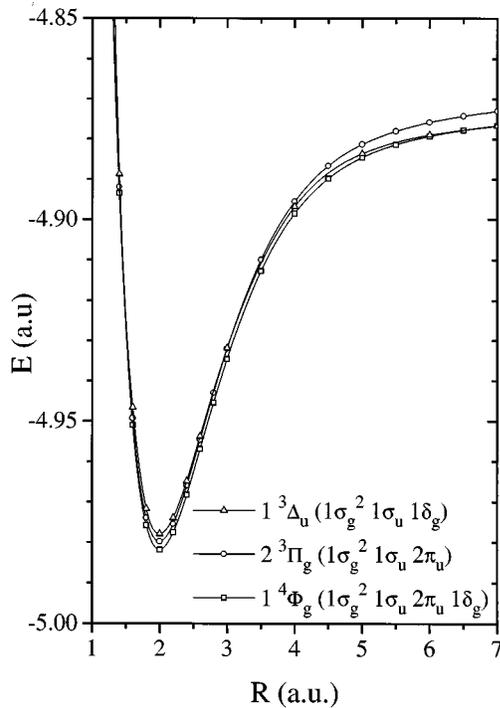


FIG. 3. The NHF energy as a function of the internuclear separation  $R$  (in a.u.). The neutral states  $\text{He}_2 \ 3\Pi_g : (1\sigma_g^2 1\sigma_u 2\pi_u)$  (this work), and  $\text{He}_2 \ 3\Delta_u : (1\sigma_g^2 1\sigma_u 1\delta_g)$  [12] are the parents of the ionic state  $\text{He}_2^- \ 4\Phi_g : (1\sigma_g^2 1\sigma_u 2\pi_u 1\delta_g)$  (which seems to be the lowest resonance in the  $4\Phi_g$  symmetry [7]).

Cullough's program PWMCSF [9] only an outline of the variational (GRAM) calculation is given here, and more details will be given in the Appendix.

For the diatomic state of interest a CI wave function is formed, consisting of the main configuration plus (usually) single and double excitations from it to other configurations; possible lower-lying open decay channels (also determined by the GRAM method) are excluded [13].

For each excitation all linearly independent symmetry-adapted configurations are used [14].

For each configuration the Slater determinants are composed of spin orbitals derived from orthogonalization of the DMO's, each of the appropriate symmetry and nature—specified by their UAQN's ( $nlm$ ). This fixes the nature of the desired state.

For each DMO different effective nuclear charges  $z_a^*, z_b^*$  are randomly chosen in a reasonable range, and are varied. At each new  $\mathbf{z}^*$  point the diatomic one-electron Schrödinger equation is solved numerically [11], the new DMO's are produced (Appendix of Ref. [15]), are orthogonalized, and the Hamiltonian matrix is diagonalized in the CI space for the linear part of the minimization.

Then the lowest eigenvalue is led to the global minimum either by the standard global minimization strategy of simulated annealing (SA) [16], or, if the orbitals are few, by repeated random application of SA's final step, i.e., of a conventional multidimensional minimization.

With the variational (GRAM) method all states in this work have been calculated both in single and in multiconfiguration using 12 DMO's with single and double excitations from the dominant configuration.

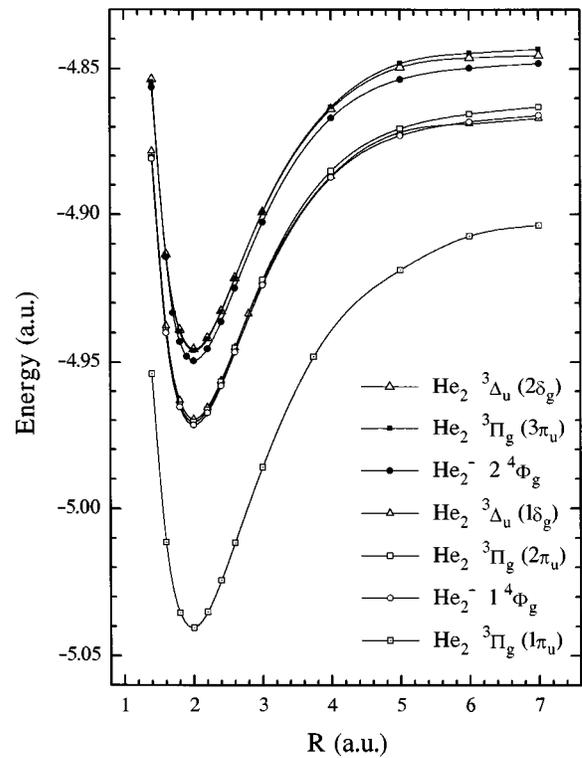


FIG. 4.  $\text{He}_2^- \ 1,4\Phi_g : (1\sigma_g^2 1\sigma_u 2\pi_u 1\delta_g)$  and  $\text{He}_2^- \ 2 \ 4\Phi_g : (1\sigma_g^2 1\sigma_u 3\pi_u 2\delta_g)$  calculated in single configuration with the GRAM method are bound with respect to their neutral parents  $\{\text{He}_2 \ 2^3\Pi_g : (1\sigma_g^2 1\sigma_u 2\pi_u), \ 1^3\Delta_u : (1\sigma_g^2 1\sigma_u 1\delta_g)\}$  and  $\{\text{He}_2 \ 3^3\Pi_g : (1\sigma_g^2 1\sigma_u 3\pi_u), \ 2^3\Delta_u : (1\sigma_g^2 1\sigma_u 2\delta_g)\}$ . The lowest  $\text{He}_2 \ 1^3\Pi_g : (1\sigma_g^2 1\sigma_u 1\pi_u)$  state is also shown.

## V. RESULTS

Both NHF and GRAM methods in single configuration exhibit the same features as it concerns the boundedness of the daughter state with respect to its neutral parents, and the relative position of the parent energy curves at large internuclear separations (where a crossing occurs). The RMS distances of the various electrons are the same in both methods. However, the NHF energies lie between the single and the multiconfiguration GRAM values (Figs. 3, 4, and 5). The NHF results are shown in Tables I and II. The GRAM results are shown in Tables III–IX. Table III shows the state  $\text{He}_2 \ 1^3\Pi_g : (1\sigma_g^2 1\sigma_u 1\pi_u)$  (calculated for completeness), Tables IV–VI refer to the first negative ionic resonance and its parents, and Tables VII–IX refer to the second negative ionic resonance and its parents.

### A. $\text{He}_2 \ 2^3\Pi_g : (1\sigma_g^2 1\sigma_u 2\pi_u)$

The total NHF energy, the orbital energies of the three orbitals,  $1\sigma_g^2, 1\sigma_u, 2\pi_u$ , and the corresponding electrons' RMS distances  $\langle R^2 \rangle^{1/2}$  of the  $2^3\Pi_g$  state, for various internuclear separations, are shown in Table I for comparison with the daughter ionic state of Ref. [7] and the other parent Ref. [12] (all are NHF calculations in single configuration). A summary from Refs. [7,12] and the present work is given in Table II. The RMS distances of the core electrons are, near equilibrium, about 1.3 a.u., whereas that of the  $2\pi_u$

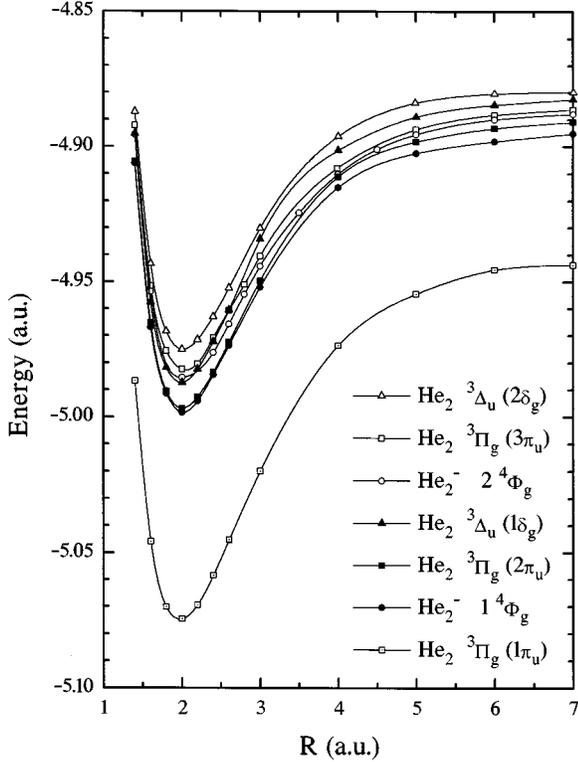


FIG. 5. Same as in Fig. 4 but with configuration interaction (CI) via the GRAM method, using 12 DMO's in single and double excitations from the main configuration.

electron is about 13 a.u., and increases with the nuclear separation less rapidly than that of the core electrons. This less rapid increase is intuitively understandable because the outer electrons, being quite far from the center, are not so sensitive to the (geometrical) details near the center. The core orbitals are almost identical in both the ionic and the parent states as shown by a comparison of the corresponding tables from Refs. [12] and [7] for the states  $1^3\Delta_u$  and  $1^4\Phi_g$ , respec-

tively (and from Table II). The outer electrons are at comparable RMS distances from the diatomic center in both of the parent states (11–13 a.u.).

Table IV shows the same  $2^3\Pi_g$  state, calculated with the GRAM method. In the CI expansion the DMO's with the following UAQN's ( $n\ell m$ ) were used: 100, 210, 311, 411, 322, 321, 422, 432, 200, 433, 310, and 543. The three leading CI terms are  $0.988(1\sigma_g^2 1\sigma_u 2\pi_u) + 0.098(1\sigma_g^2 2\sigma_u 2\pi_u) - 0.064(1\sigma_g^2 1\sigma_u 3\pi_u)$ .

### B. Boundedness of $\text{He}_2^- 1^4\Phi_g : (1\sigma_g^2 1\sigma_u 2\pi_u 1\delta_g)$

In the daughter  $\text{He}_2^-$  the outer electrons are still at comparable RMS distances from the diatomic center, which, however, are now larger (16–19 a.u.) than those of the neutral parents. This is consistent with intuition: one electron can be held closer to the nuclei than two electrons, and the two should be comparably far from the nuclei in order to form a negative ion. The  $1\delta_g$  orbital is affected slightly more than the  $2\pi_u$  orbital by the formation of the resonance. These are also indicated in Fig. 1, where it is seen that the character of the orbitals remains unchanged, while the outer electrons move farther from the nuclei in forming the negative resonance.

Figures 3 and 4 show that the  $2^3\Pi_g$  state in single configuration, either NHF or variational (GRAM), lies energetically slightly lower, by about 0.002 a.u. (Table II), than the  $1^3\Delta_u$  state at most of the internuclear separations, while their energy difference increases with CI (Fig. 5). Also in both NHF and GRAM single-configuration solutions (but not in CI) a crossing occurs at large internuclear separations,  $R_{ab} > 3.5$  a.u. However, their daughter ionic state  $1^4\Phi_g$  is bound with respect to *both* of its neutral parents at all internuclear separations ( $< 7$  a.u.), which makes it a closed channel resonance with respect to its neutral parents [17], and explains why it affects more the  $1\delta_g$  orbital of the higher neutral  $\text{He}_2 3\Delta_u$  state than the  $2\pi_u$  orbital of the energetically closer neutral  $\text{He}_2 3\Pi_g$  state. The boundedness of the ionic daughter with respect to its neutral parent states is

TABLE I. Total Hartree-Fock (NHF) energies, occupied orbital energies, and the RMS distance of the electrons from the diatomic center,  $\langle R^2 \rangle^{1/2}$ , at various internuclear separations  $R_{ab}$ , for the state  $\text{He}_2 3\Pi_g : (1\sigma_g^2 1\sigma_u 2\pi_u)$ , which is the second state in the  $3\Pi_g$  symmetry (and is one of the parent states of  $\text{He}_2^- 4\Phi_g : (1\sigma_g^2 1\sigma_u 2\pi_u 1\delta_g)$  [7]). All quantities are in a.u.

$R_{ab}$	$E_{\text{NHF}}$	$\epsilon(1\sigma_g)$	$\epsilon(1\sigma_u)$	$\epsilon(2\pi_u)$	$\langle R^2 \rangle^{1/2} (1\sigma_g)$	$\langle R^2 \rangle^{1/2} (1\sigma_u)$	$\langle R^2 \rangle^{1/2} (2\pi_u)$
1.0	-4.567284	-2.28036	-0.85448	-0.06055	0.883	1.480	12.238
1.4	-4.891906	-1.87092	-1.13123	-0.05854	1.058	1.365	12.671
1.6	-4.949317	-1.74204	-1.22571	-0.05786	1.142	1.378	12.825
1.8	-4.973932	-1.64261	-1.29564	-0.05725	1.226	1.412	12.967
2.0	-4.979795	-1.56426	-1.34649	-0.05669	1.310	1.460	13.103
2.2	-4.975439	-1.50150	-1.38292	-0.05614	1.395	1.518	13.237
2.4	-4.966022	-1.45059	-1.40858	-0.05561	1.482	1.582	13.369
2.6	-4.954608	-1.40885	-1.42627	-0.05509	1.569	1.652	13.500
3.0	-4.932002	-1.34555	-1.44551	-0.05409	1.747	1.804	13.760
4.0	-4.895515	-1.25607	-1.44989	-0.05178	2.208	2.224	14.400
5.0	-4.881303	-1.21338	-1.43837	-0.04968	2.680	2.678	15.025
6.0	-4.875795	-1.19002	-1.42786	-0.04778	3.157	3.149	15.635
7.0	-4.873041	-1.17553	-1.42038	-0.04605	3.639	3.628	16.230

TABLE II. The same quantities as in Table I at  $R_{ab} = 2$  a.u. for the lowest neutral  $\text{He}_2$   ${}^3\Pi_g:(1\sigma_g^2 1\sigma_u 1\pi_u)$  [7], the ionic  $\text{He}_2^-$   ${}^4\Phi_g:(1\sigma_g^2 1\sigma_u 2\pi_u 1\delta_g)$ , which seems to be the lowest resonance of this symmetry [7], the second neutral  $\text{He}_2$   ${}^3\Pi_g:(1\sigma_g^2 1\sigma_u 2\pi_u)$  (this work), and the lowest neutral  $\text{He}_2$   ${}^3\Delta_u:(1\sigma_g^2 1\sigma_u 1\delta_g)$  [12]. The latter two states are the parents of the above resonance. The last *four columns* represent the RMS distance of the electrons from the diatomic center.

State	$E_{\text{NHF}}$	$\epsilon(1\sigma_g)$	$\epsilon(1\sigma_u)$	$\epsilon(1\pi_u)$	$\epsilon(1\delta_g)$	$\langle 1\sigma_g \rangle$	$\langle 1\sigma_u \rangle$	$\langle \pi_u \rangle$	$\langle 1\delta_g \rangle$
$\text{He}_2$ ${}^3\Delta_u:(1\sigma_g^2 1\sigma_u 1\delta_g)$	-4.9779	-1.57	-1.35		-0.055	1.31	1.46		11.4
$\text{He}_2$ ${}^3\Pi_g:(1\sigma_g^2 1\sigma_u 2\pi_u)$	-4.9798	-1.56	-1.35	-0.057 <sup>a</sup>		1.31	1.46	13.1 <sup>a</sup>	
$\text{He}_2^-$ ${}^4\Phi_g:(1\sigma_g^2 1\sigma_u 2\pi_u 1\delta_g)$	-4.9818	-1.52	-1.30	-0.012 <sup>a b</sup>	-0.005	1.31	1.46	17.5 <sup>a b</sup>	18.8
$\text{He}_2$ ${}^3\Pi_g:(1\sigma_g^2 1\sigma_u 1\pi_u)$	-5.0512	-1.42	-1.21	-0.128 <sup>c</sup>		1.32 <sup>d</sup>	1.47 <sup>d</sup>	5.25 <sup>c</sup>	

<sup>a</sup> $2\pi_u$ .

<sup>b</sup>This orbital was assigned as  $1\pi_u$  in Ref. [7], it is actually  $2\pi_u$ .

<sup>c</sup> $1\pi_u$ .

<sup>d</sup>Not given in the literature.

probably an intrinsically natural property of the  $\text{He}_2^-$   ${}^4\Phi_g:(1\sigma_g^2 1\sigma_u 2\pi_u 1\delta_g)$  state. In order to check this further, another CI calculation, implementing a ‘‘state specific’’ technique (SST) [15] has been performed [13].

Figure 5 and Tables IV–VI show the same states calculated with the GRAM method, using 12 DMO’s in single and double excitations from the main configuration. Lower-lying open decay channels such as  $(1\sigma_g^2 1\sigma_u 2\sigma_g 1\phi_u)$  or  $(1\sigma_g 1\sigma_u^2 1\delta_g 1\pi_g)$  (in which one of the outer orbitals turns out to be much more diffuse than the other) have been excluded in order to avoid contributions from fictitious states.

The state  $\text{He}_2$   ${}^1^3\Delta_u:(1\sigma_g^2 1\sigma_u 1\delta_g)$  was calculated using the following DMO’s: 100, 210, 322, 422, 311, 321, 411, 432, 200, 433, 310, and 543. The three leading CI terms are  $0.995(1\sigma_g^2 1\sigma_u 1\delta_g) + 0.086(1\sigma_g^2 2\sigma_u 1\delta_g) + 0.031(1\sigma_u^2 2\sigma_u 1\delta_g)$ .

The state  $\text{He}_2^-$   ${}^1^4\Phi_g:(1\sigma_g^2 1\sigma_u 2\pi_u 1\delta_g)$  was calculated using the following DMO’s: 100, 210, 311, 322, 411, 422, 321, 432, 200, 433, 310, 543, and 410. The three leading CI terms are  $0.988(1\sigma_g^2 1\sigma_u 2\pi_u 1\delta_g) - 0.118(1\sigma_g^2 1\sigma_u 3\pi_u 1\delta_g) + 0.046(1\sigma_g 1\sigma_u 2\sigma_u 3\pi_u 1\delta_g)$ . The last term is, namely,

$$0.046[(1\sigma_g A 1\sigma_u A 2\sigma_u B 3\pi_u + A 1\delta_u + A) \\ + (1\sigma_g A 1\sigma_u A 2\sigma_u A 3\pi_u + A 1\delta_u + B) \\ + (1\sigma_g A 1\sigma_u A 2\sigma_u A 3\pi_u \\ + B 1\delta_u + A) - 3(1\sigma_g A 1\sigma_u B 2\sigma_u A 3\pi_u + A 1\delta_u + A)],$$

where  $A$  denotes spin up and  $B$  spin down. The orbital ‘‘+’’ sign refers to the component of the orbital angular momentum along the positive internuclear axis.

### C. $\text{He}_2^-$ $2^4\Phi_g:(1\sigma_g^2 1\sigma_u 3\pi_u 2\delta_g)$

Since  $2\pi_u$  and  $1\delta_g$  orbitals form a negative resonance, it is interesting to examine whether  $3\pi_u$  and  $2\delta_g$  can form a resonance too. Figures 4 and 5 and Tables VII–IX show that this is indeed the case:  $\text{He}_2$   ${}^3^3\Pi_g:(1\sigma_g^2 1\sigma_u 3\pi_u)$  and  $2^3\Delta_u:(1\sigma_g^2 1\sigma_u 2\delta_g)$  are the parents of  $\text{He}_2^-$   $2^4\Phi_g:(1\sigma_g^2 1\sigma_u 3\pi_u 2\delta_g)$ . They have been calculated by the GRAM method (NHF does not converge for  $2^4\Phi_g$ ) again with 12 DMO’s in single and double excitations from the main configuration.

The state  $\text{He}_2$   ${}^3^3\Pi_g:(1\sigma_g^2 1\sigma_u 3\pi_u)$  was calculated using the following DMO’s: 100, 210, 411, 431, 322, 321, 422, 432, 200, 433, 310, and 543. The three leading CI terms are  $0.967(1\sigma_g^2 1\sigma_u 3\pi_u) + 0.146(1\sigma_u^2 2\sigma_u 3\pi_u)$

TABLE III. The effective nuclear charges  $z_a^* = z_b^*$  and the RMS electron distances from the molecular center, of the DMO’s in the main configuration of  $\text{He}_2$   ${}^1^3\Pi_g:(1\sigma_g^2 1\sigma_u 1\pi_u)$ . All quantities are in atomic units.

$R_{ab}$	$z^*(1\sigma_g)$	$z^*(1\sigma_u)$	$z^*(1\pi_u)$	$\langle R^2 \rangle^{1/2}(1\sigma_g)$	$\langle R^2 \rangle^{1/2}(1\sigma_u)$	$\langle R^2 \rangle^{1/2}(1\pi_u)$
1.4	1.29642	1.85263	0.52943	1.049	1.317	5.219
1.6	1.25639	1.94837	0.55688	1.133	1.340	5.014
1.8	1.23325	2.00897	0.54722	1.218	1.381	5.109
2.0	1.23821	2.05299	0.53644	1.297	1.435	5.211
2.2	1.21671	2.09476	0.53005	1.385	1.496	5.279
2.4	1.21553	2.13586	0.53012	1.470	1.563	5.299
2.6	1.21883	2.18375	0.53017	1.556	1.635	5.321
3.0	1.23663	2.28071	0.53023	1.733	1.789	5.369
4.0	1.27911	2.49205	0.53031	2.194	2.210	5.517
5.0	1.29155	2.57736	0.53031	2.667	2.634	5.701
6.0	1.26053	2.58121	0.53031	3.146	3.112	5.919
7.0	1.19009	2.58116	0.53031	3.629	3.599	6.171

TABLE IV. Same as in Table III but for  $\text{He}_2 \ 2^3\Pi_g : (1\sigma_g^2 1\sigma_u 2\pi_u)$ .

$R_{ab}$	$z^*(1\sigma_g)$	$z^*(1\sigma_u)$	$z^*(2\pi_u)$	$\langle R^2 \rangle^{1/2} (1\sigma_g)$	$\langle R^2 \rangle^{1/2} (1\sigma_u)$	$\langle R^2 \rangle^{1/2} (2\pi_u)$
1.4	1.32355	1.85324	0.54771	1.045	1.314	12.535
1.6	1.28404	1.91326	0.54417	1.129	1.337	12.689
1.8	1.25813	1.96756	0.54124	1.213	1.379	12.835
2.0	1.24213	2.02005	0.53850	1.297	1.432	12.981
2.2	1.23498	2.07262	0.53594	1.381	1.493	13.128
2.4	1.23476	2.12569	0.53359	1.466	1.560	13.273
2.6	1.24045	2.17941	0.53137	1.553	1.632	13.418
3.0	1.26154	2.28803	0.52753	1.730	1.786	13.703
4.0	1.36075	2.54165	0.52039	2.188	2.210	14.386
5.0	1.41552	1.83596	0.51544	2.662	2.651	15.040
6.0	1.37150	1.83602	0.51284	3.143	3.127	15.645
7.0	1.30678	1.83602	0.51095	3.627	3.611	16.234

$-0.136 (1\sigma_g 1\sigma_u 2\sigma_g 3\pi_u)$ , where the last term is, namely,  $-0.136[(1\sigma_g A 1\sigma_u A 2\sigma_g B 3\pi_u + A) + (1\sigma_g A 1\sigma_u A 2\sigma_g A 3\pi_u + B) + (1\sigma_g A 1\sigma_u B 2\sigma_g A 3\pi_u + A) - 3(1\sigma_g B 1\sigma_u A 2\sigma_g A 3\pi_u + A)]$ . The state  $\text{He}_2 \ 2^3\Delta_u : (1\sigma_g^2 1\sigma_u 2\delta_g)$  was calculated using the following DMO's: 100, 210, 422, 522, 311, 321, 411, 432, 200, 433, 310, and 543. The three leading CI terms are  $0.971 (1\sigma_g^2 1\sigma_u 2\delta_g) - 0.136 (1\sigma_g 1\sigma_u 2\sigma_g 2\delta_g) - 0.114 (1\sigma_g^2 2\sigma_u 2\delta_g)$ . The second term is, namely,  $-0.136[(1\sigma_g A 1\sigma_u A 2\sigma_g B 2\delta_g + A) + (1\sigma_g A 1\sigma_u A 2\sigma_g A 2\delta_g + B) + (1\sigma_g A 1\sigma_u B 2\sigma_g A 2\delta_g + A) - 3(1\sigma_g B 1\sigma_u A 2\sigma_g A 2\delta_g + A)]$ .

The state  $\text{He}_2^- \ 2^4\Phi_g : (1\sigma_g^2 1\sigma_u 3\pi_u 2\delta_g)$  was calculated using the following DMO's: 100, 210, 411, 422, 431, 522, 321, 432, 200, 433, 310, 543, and 410. The three leading CI terms are

$$0.972 (1\sigma_g^2 1\sigma_u 3\pi_u 2\delta_g) + 0.130 (1\sigma_g 1\sigma_u 2\sigma_g 3\pi_u 2\delta_g) + 0.108 (1\sigma_g 1\sigma_u 2\sigma_g 3\pi_u 2\delta_g),$$

where the last two terms are actually

$$0.130[(1\sigma_g A 1\sigma_u A 2\sigma_g B 3\pi_u + A 2\delta_g + A) + (1\sigma_g A 1\sigma_u A 2\sigma_g A 3\pi_u + A 2\delta_g + B) + (1\sigma_g A 1\sigma_u A 2\sigma_g A 3\pi_u + B 2\delta_g + A) + (1\sigma_g A 1\sigma_u B 2\sigma_g A 3\pi_u + A 2\delta_g + A) - 4(1\sigma_g B 1\sigma_u A 2\sigma_g A 3\pi_u + A 2\delta_g + A)] + 0.108[(1\sigma_g A 1\sigma_u A 2\sigma_g B 3\pi_u + A 2\delta_g + A) - (1\sigma_g A 1\sigma_u A 2\sigma_g A 3\pi_u + A 2\delta_g + B)].$$

The ionic daughter  $2^4\Phi_g$  is also bound with respect to both of its neutral parents. The RMS distances of the resonating electrons from the diatomic center are 24 a.u. in the  $3\pi_u$  and 23 a.u. in the  $2\delta_g$  orbitals of the neutral parents, whereas they increase to 32 and 33 a.u., respectively in the negative daughter. The core orbitals  $1\sigma_g$  and  $1\sigma_u$  still remain similar to those of  $1^4\Phi_g$ .

#### D. Does $\text{He}_2^- \ 4\Phi_g : (1\sigma_g^2 1\sigma_u 1\pi_u 1\delta_g)$ exist?

The first neutral  $\text{He}_2 \ 3\Pi_g : (1\sigma_g^2 1\sigma_u 1\pi_u)$  state lies as much as 0.070 a.u. lower than  $1^4\Phi_g$  and its parents (Figs. 4 and 5). With the GRAM method it was calculated using

TABLE V. Same as in Table III but for  $\text{He}_2 \ 1^3\Delta_u : (1\sigma_g^2 1\sigma_u 1\delta_g)$ .

$R_{ab}$	$z^*(1\sigma_g)$	$z^*(1\sigma_u)$	$z^*(1\delta_g)$	$\langle R^2 \rangle^{1/2} (1\sigma_g)$	$\langle R^2 \rangle^{1/2} (1\sigma_u)$	$\langle R^2 \rangle^{1/2} (1\delta_g)$
1.4	1.32449	1.85604	0.50138	1.044	1.313	11.276
1.6	1.28772	1.91509	0.50049	1.129	1.336	11.323
1.8	1.26270	1.96889	0.49946	1.212	1.378	11.368
2.0	1.24755	2.02131	0.49899	1.296	1.431	11.412
2.2	1.24077	2.07485	0.49851	1.380	1.492	11.455
2.4	1.24120	2.12686	0.49817	1.465	1.560	11.499
2.6	1.24742	2.18057	0.49791	1.552	1.631	11.542
3.0	1.27278	2.28897	0.49769	1.729	1.785	11.630
4.0	1.36479	2.54306	0.49744	2.187	2.209	11.865
5.0	1.42977	2.66476	0.49681	2.661	2.647	12.142
6.0	1.38532	1.82951	0.49764	3.142	3.127	12.436
7.0	1.32105	1.82951	0.49768	3.626	3.611	12.757

TABLE VI. Similar to Table III but for  $\text{He}_2^- 1^4\Phi_g:(1\sigma_g^2 1\sigma_u 2\pi_u 1\delta_g)$ .

$R_{ab}$	$z^*(1\sigma_g)$	$z^*(1\sigma_u)$	$z^*(2\pi_u)$	$z^*(1\delta_g)$	$\langle R^2 \rangle^{1/2} (1\sigma_g)$	$\langle R^2 \rangle^{1/2} (1\sigma_u)$	$\langle R^2 \rangle^{1/2} (2\pi_u)$	$\langle R^2 \rangle^{1/2} (1\delta_g)$
1.4	1.32520	1.85413	0.42577	0.30428	1.044	1.313	15.794	18.459
1.6	1.28602	1.91419	0.42185	0.30299	1.129	1.337	15.951	18.541
1.8	1.26047	1.96824	0.41827	0.30176	1.213	1.378	16.100	18.621
2.0	1.24370	2.02058	0.41473	0.30056	1.297	1.432	16.251	18.700
2.2	1.23772	2.07339	0.41120	0.29934	1.381	1.493	16.404	18.782
2.4	1.23797	2.12622	0.40769	0.29814	1.466	1.560	16.560	18.863
2.6	1.24395	2.17991	0.40424	0.29695	1.552	1.632	16.717	18.945
3.0	1.26541	2.28829	0.39747	0.29456	1.729	1.786	17.038	19.113
4.0	1.36649	2.54213	0.38197	0.28860	2.188	2.209	17.840	19.550
5.0	1.42451	1.83648	0.37296	0.28233	2.662	2.647	18.556	20.034
6.0	1.38324	1.83654	0.37913	0.27433	3.143	3.127	19.288	20.674
7.0	1.30552	1.83654	0.37388	0.26762	3.627	3.611	19.976	21.258

the following DMO's: 100, 210, 211, 311, 322, 321, 422, 432, 200, 433, 310, and 543. The first three leading terms in the CI expansion are  $0.986 (1\sigma_g^2 1\sigma_u 1\pi_u) - 0.102(1\sigma_g^2 2\sigma_u 1\pi_u) - 0.061(1\sigma_g 1\sigma_u 2\sigma_g 1\pi_u)$ . The last term is actually

$$\begin{aligned}
& -0.061[(1\sigma_g A 1\sigma_u A 2\sigma_g B 1\pi_u + A) \\
& + (1\sigma_g A 1\sigma_u A 2\sigma_g A 1\pi_u + B) \\
& - 2(1\sigma_g A 1\sigma_u B 2\sigma_g A 1\pi_u + A)].
\end{aligned}$$

There remains an open question whether a lower ionic  $\text{He}_2^- 1^4\Phi_g:(1\sigma_g^2 1\sigma_u 1\pi_u 1\delta_g)$  state exists, which would have as parents  $\text{He}_2 1^3\Pi_g: [(1\sigma_g^2 1\sigma_u 1\pi_u), -5.05, 5]$  and  $\text{He}_2 1^3\Delta_u: [(1\sigma_g^2 1\sigma_u 1\delta_g), -4.98, 12]$ . NHF does not find this state. Considering the RMS distances in the parents, it is anticipated that it is unlikely that the two outer orbitals, while retaining their character  $1\pi_u$  and  $1\delta_g$ , may be so much deformed so as to keep the outer electrons at comparable separations from the nuclei in order to form the desired negative ion. Therefore, it is expected that this state does not exist. Nevertheless this needs a proof. [A proof is under consideration [18] via the variational (GRAM) method, based on the fact that at the *global* energy minimum of  $\text{He}_2^- 1^4\Phi_g:(1\sigma_g^2 1\sigma_u 1\pi_u 1\delta_g)$ , one of the orbitals,  $1\pi_u$ , has finite

effective nuclear charges, whereas in the other one,  $1\delta_g$ , both effective nuclear charges are zero,  $z_a^* = z_b^* = 0 (< 10^{-6})$ , which means that the corresponding electron ‘‘rests’’ at infinity. Hence the variational calculation predicts [18] that  $\text{He}_2^- 1^4\Phi_g:(1\sigma_g^2 1\sigma_u 1\pi_u 1\delta_g)$  cannot be formed, since the *global* minimum with energy  $E = -5.04$  a.u. merely tries to describe a neutral  $\text{He}_2 1^3\Pi_g:(1\sigma_g^2 1\sigma_u 1\pi_u)$  with an electron at infinity in a  $1\delta_g$  type orbital.]

## VI. SUMMARY

In conclusion, after proving that the neutral  $\text{He}_2$  states, reported as parent states of  $\text{He}_2^- 1^4\Phi_g$  in Ref. [7] are incorrect, it is shown that (a) the  $\text{He}_2^- 1^4\Phi_g$  state of Ref. [7] has a  $2\pi_u$  instead of  $1\pi_u$  orbital, as claimed in Ref. [7], (b) the  $\text{He}_2^- 1^4\Phi_g$  is a closed channel ‘‘Feshbach’’ type negative ion resonance, below  $\text{He}_2 2^3\Pi_g$  and  $1^3\Delta_u$ , (c) the  $\text{He}_2^- 2^4\Phi_g$  is also a similar closed channel negative ion resonance, below  $\text{He}_2 3^3\Pi_g$  and  $2^3\Delta_u$ , and (d)  $\text{He}_2^- 1^4\Phi_g:(1\sigma_g^2 1\sigma_u 1\pi_u 1\delta_g)$  does not exist. The relevant  $\text{He}_2$  and  $\text{He}_2^-$  states are as follows:  $\text{He}_2 1^3\Pi_g:(1\sigma_g^2 1\sigma_u 1\pi_u)$  at  $E_0 = -5.05$  a.u. (at  $R = 2$  a.u.);  $\text{He}_2 2^3\Pi_g:(1\sigma_g^2 1\sigma_u 2\pi_u)$  and  $1^3\Delta_u:(1\sigma_g^2 1\sigma_u 1\delta_g)$  as well as their ionic daughter  $\text{He}_2^- 1^4\Phi_g:(1\sigma_g^2 1\sigma_u 2\pi_u 1\delta_g)$  at  $E_0 = -4.98$  a.u.;  $\text{He}_2 3^3\Pi_g:(1\sigma_g^2 1\sigma_u 3\pi_u)$  and  $2^3\Delta_u:(1\sigma_g^2 1\sigma_u 2\delta_g)$  with their

TABLE VII. Same as in Table III but for  $\text{He}_2 3^3\Pi_g:(1\sigma_g^2 1\sigma_u 3\pi_u)$ .

$R_{ab}$	$z^*(1\sigma_g)$	$z^*(1\sigma_u)$	$z^*(3\pi_u)$	$\langle R^2 \rangle^{1/2} (1\sigma_g)$	$\langle R^2 \rangle^{1/2} (1\sigma_u)$	$\langle R^2 \rangle^{1/2} (3\pi_u)$
1.4	1.30561	1.80839	0.48821	1.047	1.312	25.131
1.6	1.26689	1.91597	0.52445	1.131	1.337	23.518
1.8	1.26157	1.99781	0.52050	1.211	1.379	23.719
2.0	1.24869	2.04898	0.51688	1.295	1.432	23.907
2.2	1.24161	2.09308	0.51338	1.381	1.493	24.089
2.4	1.24460	2.13857	0.50982	1.465	1.560	24.273
2.6	1.25127	2.18725	0.50635	1.552	1.632	24.451
3.0	1.27808	2.28683	0.49981	1.729	1.785	24.787
4.0	1.35049	2.50408	0.48907	2.189	2.205	25.373
5.0	1.36084	2.59556	0.48912	2.666	2.634	25.537
6.0	1.39380	2.59992	0.48919	3.142	3.112	25.725
7.0	1.36361	2.60007	0.48919	3.626	3.599	25.937

TABLE VIII. Same as in Table III but for  $\text{He}_2 \ 2^3\Delta_u : (1\sigma_g^2 1\sigma_u 2\delta_g)$ .

$R_{ab}$	$z^*(1\sigma_g)$	$z^*(1\sigma_u)$	$z^*(2\delta_g)$	$\langle R^2 \rangle^{1/2} (1\sigma_g)$	$\langle R^2 \rangle^{1/2} (1\sigma_u)$	$\langle R^2 \rangle^{1/2} (2\delta_g)$
1.4	1.30642	1.80826	0.45792	1.047	1.312	24.533
1.6	1.26755	1.91591	0.49861	1.131	1.337	22.576
1.8	1.26207	1.99812	0.49751	1.211	1.378	22.641
2.0	1.24894	2.04957	0.49647	1.295	1.432	22.704
2.2	1.24369	2.09351	0.49547	1.380	1.493	22.767
2.4	1.24683	2.13911	0.49453	1.465	1.560	22.828
2.6	1.25374	2.18779	0.49363	1.551	1.632	22.889
3.0	1.28009	2.28746	0.49187	1.728	1.785	23.012
4.0	1.34539	2.50537	0.48761	2.190	2.205	23.325
5.0	1.36463	2.59604	0.48257	2.666	2.634	23.679
6.0	1.38113	2.60197	0.47779	3.144	3.112	24.026
7.0	1.38698	2.60072	0.47300	3.624	3.599	24.371

ionic daughter  $\text{He}_2^- \ 2^4\Phi_g : (1\sigma_g^2 1\sigma_u 3\pi_u 2\delta_g)$  at  $E_0 = -4.95$  a.u. It is anticipated that the whole series of the ionic  $^4\Phi_g$  daughters would be formed from the  $^3\Pi_g$  and  $^3\Delta_u$  neutral parents with  $(n+1)\pi_u$  and  $n\delta_g$  orbitals, provided that their RMS extents are comparable. Finally it might be said that the GRAM method is a useful technique for finding stable diatomic states.

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#### APPENDIX: THE GRAM METHOD

The diatomic  $n$ -electron normalized wave function is approximated by a CI expansion consisting of  $n_{\text{conf}}$  configurations:

$$\Psi(x_1, x_2, \dots, x_n) = \sum_{p=1}^{n_{\text{conf}}} c_p \Phi_p(x_1, x_2, \dots, x_n), \quad (\text{A1})$$

$$\{x\} = \{(\mathbf{r}, s)\}, \quad (\text{A2})$$

$$|\Psi|^2 = 1, \quad (\text{A3})$$

$$\Phi_p = \sum_I a_{I,p} D_I, \quad (\text{A4})$$

where  $D_I$  are Slater determinants composed of given parametrized orthonormal spin orbitals,  $u_i(\mathbf{r}_k)\alpha$  (for spin up or  $\beta$  for spin down), and  $a_{I,p}$  are their fixed coefficients determining the symmetry of the state. Each configuration is usually formed by single and double excitations from a main configuration, and for each excitation all linearly independent symmetry-adapted configurations are calculated by the QCPE program HEDIAG [14], appropriately expanded here so as to give small integer (unnormalized) Slater determinant coefficients based on the orthogonal basis  $\{(1,1,1,1,1,\dots), (1,-1,0,0,0,\dots), (1,1,-2,0,0,\dots), (1,1,1,-3,0,0,\dots), \dots\}$ ; [the first vector belongs to a one-dimensional subspace, orthogonal to the subspace spanned by the remaining (degenerate) vectors].

The problem is to determine which values of the  $c_p$  coefficients and of the spin orbital parameters minimize the expectation value of the two center  $(a,b)$  Hamiltonian,  $E = \langle \Psi | H | \Psi \rangle$ .

Since

$$H = \sum_{i=1}^n h_i + \sum_{i>j}^n \frac{1}{r_{ij}}, \quad (\text{A5})$$

$$h_i = -\nabla_i^2 - Z_a/r_{ai} - Z_b/r_{bi}, \quad (\text{A6})$$

TABLE IX. Same as Table VI but for  $\text{He}_2^- \ 2^4\Phi_g : (1\sigma_g^2 1\sigma_u 3\pi_u 2\delta_g)$ .

$R_{ab}$	$z^*(1\sigma_g)$	$z^*(1\sigma_u)$	$z^*(3\pi_u)$	$z^*(2\delta_g)$	$\langle R^2 \rangle^{1/2} (1\sigma_g)$	$\langle R^2 \rangle^{1/2} (1\sigma_u)$	$\langle R^2 \rangle^{1/2} (3\pi_u)$	$\langle R^2 \rangle^{1/2} (2\delta_g)$
1.4	1.30456	1.75378	0.36832	0.32894	1.048	1.309	33.286	34.139
1.6	1.33092	1.84432	0.36839	0.32901	1.114	1.335	33.290	34.136
2.0	1.34766	2.03525	0.38652	0.33895	1.264	1.433	31.757	33.147
2.4	1.34766	2.03525	0.38652	0.33895	1.431	1.600	31.788	33.160
2.6	1.34766	2.03525	0.38652	0.33895	1.518	1.687	31.805	33.168
3.0	1.34766	2.23659	0.38652	0.33902	1.699	1.781	31.843	33.178
4.0	1.93825	2.50879	0.38652	0.33909	2.140	2.205	31.957	33.223
5.0	1.93825	2.59720	0.38652	0.33916	2.625	2.633	32.096	33.281
6.0	1.93825	2.60207	0.38652	0.33922	3.110	3.112	32.258	33.354
7.0	1.93825	2.60207	0.38652	0.33922	3.597	3.599	32.440	33.445

where  $Z_a, Z_b$  are the nuclear charges and  $r_{xy}$  is the distance between the particles  $x$  and  $y$ , then

$$E = \sum_{p,q} c_p c_q H_{p,q}, \quad (\text{A7})$$

$$H_{p,q} = \sum_{s_1, \dots, s_n} \int d\tau_1 \dots d\tau_n \Phi_p^* H \Phi_q \quad (\text{A8})$$

$$= \sum_{I,J} a_{I,p} a_{J,q} \langle D_I | H | D_J \rangle. \quad (\text{A9})$$

The matrix elements  $\langle D_I | H | D_J \rangle$  are reduced to one- and

two-electron integrals according to the number of different spin orbitals in  $D_I$  and  $D_J$  [19].

The Hamiltonian and the spin orbitals are calculated in prolate spheroidal coordinates  $\mathbf{r} = (\xi, \eta, \phi)$  (see, for example, the Appendix of Ref. [9] and references therein)

$$\xi = (r_a + r_b)/R, \xi \geq 1; \quad (\text{A10})$$

$$\eta = (r_a - r_b)/R, |\eta| \leq 1, \quad (\text{A11})$$

where  $r_x$  is the distance from center  $x$ ,  $R$  is the internuclear distance, and  $\phi$  is the azimuthal angle,  $0 \leq \phi \leq 2\pi$ , with

$$d\tau = \frac{R^3}{8} (\xi^2 - \eta^2) d\xi d\eta d\phi, \quad (\text{A12})$$

$$\nabla^2 = \frac{4}{(R^2(\xi^2 - \eta^2))} \left[ \frac{\partial}{\partial \xi} (\xi^2 - 1) \frac{\partial}{\partial \xi} + \frac{\partial}{\partial \eta} (1 - \eta^2) \frac{\partial}{\partial \eta} + \left( \frac{1}{(\xi^2 - 1)} + \frac{1}{(1 - \eta^2)} \right) \frac{\partial^2}{\partial \phi^2} \right], \quad (\text{A13})$$

$$\frac{1}{r_{12}} = \frac{8\pi}{R} \sum_{\lambda=0}^{\infty} \sum_{\mu=-\lambda}^{\lambda} (-1)^{\mu} \frac{(\lambda - |\mu|)!}{(\lambda + |\mu|)!} P_{\lambda}^{|\mu|}(\min\{\xi_1, \xi_2\}) Q_{\lambda}^{|\mu|}(\max\{\xi_1, \xi_2\}) Y_{\lambda}^{\mu}(\eta_1, \phi_1) Y_{\lambda}^{\mu}(\eta_2, \phi_2)^*, \quad (\text{A14})$$

where  $P_{\lambda}^{|\mu|}(x)$  and  $Q_{\lambda}^{|\mu|}(x)$  are the associated Legendre functions of the first and second kind, defined as  $P_{\lambda}^{|\mu|}(x) = |x^2 - 1|^{|\mu|/2} d^{|\mu|} P_{\lambda} / dx^{|\mu|}$  [9,20,21] and  $Y_{\lambda}^m(\eta, \phi) = [(2\lambda + 1)(\lambda - |m|)! / 4\pi(\lambda + |m|)!]^{1/2} P_{\lambda}^{|\mu|}(\eta) e^{im\phi}$  are spherical harmonics. Usually, depending on  $R$ , about 10 values of  $\lambda$  are used.

$P_{\lambda}^m(z)$  is calculated as suggested on p. 182 of Ref. [22].  $Q_{\lambda}^m(\xi)$ , for  $\xi = 1/z^2 > 1$ , is calculated as defined on p. 332 of Ref. [23] in terms of the hypergeometric function  $F_{21}$  in  $(0,1)$ , which, for  $z < 0.1$ , is computed as a series expansion for positive or negative  $m$ , and for  $z > 0.9$  is computed by reflection formulas around 0.5 (pp. 556 and 559 of Ref. [23]). The gamma and digamma functions involved are as easily computable as, say,  $e^x$  (p. 157 of Ref. [22]); for  $0.1 < z < 0.9$ ,  $F_{21}$  is computed by direct integration of its differential equation as suggested on p. 563 of Ref. [22].

The spin orbitals are composed of DMO's  $\psi(\mathbf{r}) = \Xi(\xi) H(\eta) e^{im\phi}$ , computed as discussed in the Appendix of Ref. [15], orthonormalized by the Gram-Schmidt method: The orthogonal basis is given in terms of the nonorthogonal by  $|u_n\rangle = |\psi_n\rangle - \sum_{i=1}^{n-1} |\psi_i\rangle c_{in}$  where the transformation matrix  $c_{in}$  is built up by  $\{[(c_{in} = A_{in} - \sum_{k=i+1}^{n-1} c_{ik} A_{kn}) \ i = 1, n-1] \ n = 2, n_{\text{orb}}\}$  and the (inverse) matrix  $A_{kn}$  is built up by  $\{[(\langle u_j | u_j \rangle = \langle \psi_j | \psi_j \rangle - \sum_{i=1}^{j-1} \langle u_i | u_i \rangle A_{ij}^2), \ [(\langle u_j | u_j \rangle A_{jn} = \langle \psi_j | \psi_n \rangle - \sum_{i=1}^{j-1} \langle u_i | u_i \rangle A_{ij} A_{in}) \ n = j+1, n_{\text{orb}}] \ j = 1, n_{\text{orb}}\}$ . Here  $n_{\text{orb}}$  is the number of orbitals.

The DMO's obey [11] the separate differential equations,

$$\frac{d}{d\xi} \left[ (\xi^2 - 1) \frac{d\Xi(\xi)}{d\xi} \right] = \left[ \frac{m^2}{(\xi^2 - 1)} + c + p^2(\xi^2 - 1) - R(z_a^* + z_b^*)\xi \right] \Xi(\xi), \quad (\text{A15})$$

$$\frac{d}{d\eta} \left[ (1 - \eta^2) \frac{dH(\eta)}{d\eta} \right] = \left[ \frac{m^2}{(1 - \eta^2)} - c + p^2(1 - \eta^2) + R(z_a^* - z_b^*)\eta \right] H(\eta), \quad (\text{A16})$$

where  $c, p$  (calculated by Power's QCPE program OEDM [11]) and  $m$  are the separation constants, and  $z^*$ , the effective nuclear charges, are used as nonlinear variational parameters. These equations will be used in the evaluation of the total kinetic energy.

With the Hamiltonian and the spin orbitals expressed in prolate spheroidal coordinates it remains to calculate the Hamiltonian matrix elements. It is straightforward to show the following.

The overlap integrals in terms of DMO's are

$$\langle \psi' | \psi \rangle = \frac{2\pi R^3}{8} \delta_{m',m} \left[ \int d\eta H' H \int d\xi \xi^2 \Xi' \Xi - \int d\xi \Xi' \Xi \int d\eta \eta^2 H' H \right]. \quad (\text{A17})$$

The one-electron integrals, if  $z = Z_a + Z_b$ ,  $\zeta = Z_a - Z_b$ ,  $z^* = z_a^* + z_b^*$ , and  $\zeta^* = z_a^* - z_b^*$ , in view of the DMO differential equations (A15), (A16), are

$$\langle \psi' | h | \psi \rangle = -\frac{2\pi R}{4} \delta_{m',m} \int d\xi d\eta \Xi' \Xi H' H [p^2(\xi^2 - \eta^2) + R(z - z^*)\xi - R(\zeta - \zeta^*)\eta], \quad (\text{A18})$$

which are again of the form  $\int d\eta H' H \int d\xi A(\xi) \Xi' \Xi - \int d\xi \Xi' \Xi \int d\eta B(\eta) H' H$ .

For the two-electron integrals  $\langle \psi_i \psi_j | 1/r_{12} | \psi_k \psi_l \rangle$ , by denoting for each  $i, k, \lambda$ , and  $\mu$ :

$$a\xi^2 + b = \int d\eta (\xi^2 - \eta^2) H_i(\eta) H_k(\eta) P_\lambda^{|\mu|}(\eta), \quad (\text{A19})$$

$$S_{i,k,\lambda}^\mu(\xi) = \Xi_i(\xi) \Xi_k(\xi) (a\xi^2 + b), \quad (\text{A20})$$

the terms surviving from  $\delta_{m_i, m_k + \mu}$  are of the form

$$\int_1^\infty d\xi_1 S_{i,k,\lambda}^\mu(\xi_1) \left[ Q_\lambda^\mu(\xi_1) \int_1^{\xi_1} d\xi_2 S_{j,l,\lambda}^\mu(\xi_2) P_\lambda^\mu(\xi_2) + P_\lambda^\mu(\xi_1) \int_{\xi_1}^\infty d\xi_2 S_{j,l,\lambda}^\mu(\xi_2) Q_\lambda^\mu(\xi_2) \right]. \quad (\text{A21})$$

Thus the interelectronic repulsion is reflected in a logarithmic singularity of  $Q(1)$ , which is accurately integrated by a numerical change of variable, i.e., by finding the root of  $x \ln(x) - x = -t$  in  $(0,1)$ . All integrals are performed by an adaptive step method, i.e., by subdividing, if necessary, each interval into two parts, and by comparing the total with the sum of the left and right parts. In every interval a Newton-Cotes formula using four equal subdivisions is used, i.e.,  $[7f_1 + 32f_2 + 12f_3 + 32f_4 + 7f_5](x_5 - x_1)/90$ .

The standard linear variation leads to a secular equation, whose lowest root is led to minimum by varying the nonlinear parameters, i.e., the DMO effective nuclear charges.

The global minimum is found by a standard method of global minimization, namely, by simulated annealing [16], i.e., by accepting the energy at a new point, randomly close to the old one, with probability  $e^{-(E_{\text{new}} - E_{\text{old}})/T}$ , where  $T$  is an external parameter, "temperature," diminished to zero with a "slow" strategy; the determination of "slow" cooling usually needs experimentation; for example, after  $E$  is adequately stabilized on the average for each  $T$ ,  $T$  may be reduced by 5%. (Thus high  $T$ 's give the system an opportunity to escape from around a local minimum and visit other local minima, and low  $T$ 's almost never raise the system away from a local minimum. If cooling is "fast," a local minimum, "polycrystalline," will be reached. If it is "slow" the system will have the time to reach the global "mono-crystalline" minimum and stay there.) When  $T$  becomes small enough (say 0.5% of the maximum energy range observed), minimization is concluded conventionally, via Powell's method of conjugate directions (p. 297 in Ref. [22]), restricted here to positive effective nuclear charges.

However, when the number of orbitals is small, experience shows that there are few local minima more or less distinct from each other. In this case all local minima, and in particular the global one, can be found by repeated random application of the conventional minimization, i.e., by randomly choosing many (say 100) points in the DMO effective nuclear charge space, and by finding for each of them the energy minimum closest to it. This procedure is denoted as global randomly applied minimization (GRAM), and was applied here in order to verify the boundedness of the ionic  $\text{He}_2^- 1^4\Phi_g$  with respect to its neutral parents  $\text{He}_2 2^3\Pi_g$  and  $1^3\Delta_u$  and to obtain the second ionic  $2^4\Phi_g$  and its neutral parents.

The global (randomly applied) energy minimization (GRAM), via simultaneous variation of the DMO's involved in a CI expansion, has not been fully exploited yet as a general method, but preliminary results from this work and from Ref. [18] suggest that it turns out to be a very powerful method for diatomic molecules. It seems to be able to calculate any desired diatomic state, excited or not, since it does not depend on successful convergence of nonlinear iterative schemes like Hartree-Fock; it rather keeps track of the intuitive nature of the desired state. If the state exists, the GRAM method provides the correct result, and if it yields an unphysical result it suggests that the state should not exist. When the CI expansion chosen (for an existing state) is small (e.g., single configuration), then the GRAM method is generally inferior to the NHF (if the latter converges). The larger the CI expansion the more GRAM tends to a multiconfiguration NHF. However, the CI expansion need not be huge because the description never departs from the natural character of the desired state.

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