# Lowest ${ }^{3} \Delta_{u}$ state of $\mathrm{He}_{\mathbf{2}}$ 

N. C. Bacalis<br>Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, Vassileos Constantinou 48, GR - 11635 Athens, Greece

(Received 24 August 1992)
The $\mathrm{He}_{2}$ molecule is examined in the ${ }^{3} \Delta_{u}$ symmetry via the numerical Hartree-Fock method. A previously unreported state is found with lower energy than states reported in the literature, necessitating a reassessment of the question of the stability of corresponding "daughter" states of the $\mathrm{He}_{2}{ }^{-}$ion.

PACS number(s): 31.20.Di, 31.20.Ej, 31.50.+w

The $\mathrm{He}_{2}$ - ion has been reported to be relatively stable in two metastable states, ${ }^{4} \Pi_{g}[1]$ and ${ }^{4} I_{g}[2]$. Both are characterized by the same $\mathrm{He}_{2}+$ core $\left(1 \sigma_{g}^{2} 1 \sigma_{u}\right)$ to which the two outer electrons are attached in diffuse bonding orbitals of consecutive angular-momentum quantum numbers. The relative stability of these states is determined with respect to their "parent" states of the neutral $\mathrm{He}_{2}$ molecule.

In examining the relative stability of the metastable states ${ }^{4} \Phi_{g}$ and ${ }^{4} I_{g}$ of the $\mathrm{He}_{2}$ - ion Adamowicz and Pluta [2] have calculated self-consistently the corresponding parent states of $\mathrm{He}_{2}{ }^{3} \Pi_{g},{ }^{3} \Delta_{u}$, and ${ }^{3} \Phi_{g}$, by the computer program PWMCSCF of McCullough and Adamowicz [3], in the single-configuration restricted HartreeFock approximation, where the corresponding configurations are $\mathrm{He}_{2}-{ }^{4} \Phi_{g}:\left(1 \sigma_{g}^{2} 1 \sigma_{u} 1 \pi_{u} 1 \delta_{g}\right), \mathrm{He}_{2}-{ }^{4} I_{g}$ : $\left(1 \sigma_{g}^{2} 1 \sigma_{u} 1 \delta_{g} 1 \phi_{u}\right)$; and the parent states: $\mathrm{He}_{2}{ }^{3} \Pi_{g}$ : $\left(1 \sigma_{g}^{2} 1 \sigma_{u} 1 \pi_{u}\right)$, $\mathrm{He}_{2}{ }^{3} \Delta_{u}:\left(1 \sigma_{g}^{2} 1 \sigma_{u} 1 \delta_{g}\right)$, and $\mathrm{He}_{2}{ }^{3} \Phi_{g}$ : $\left(1 \sigma_{g}^{2} 1 \sigma_{u} 1 \phi_{u}\right)$. In all of these states the first two orbitals are very similar to the ones of the $\mathrm{He}_{2}+{ }^{2} \Sigma_{u}^{+}$: ( $1 \sigma_{g}^{2} 1 \sigma_{u}$ ) state, while the outer orbitals are quite diffuse in both the parent neutral and the ionic states. Typical values reported [2] for the total energy of the neutral $\mathrm{He}_{2}$ molecule, its orbital energies, and the squared distance $\left\langle R^{2}\right\rangle$ of the outer electron from the center of the molecule are shown in Table I for the equilibrium internuclear separation ( $R_{a b}=2$ a.u.). The self-consistent-field (SCF) calculation converges to these values starting from reasonable initial guesses. However, the results emerging from the $1 \delta_{g}$ orbital exhibit the unexpected feature that they do not lie between those arising from the $1 \pi_{u}$ and the $1 \phi_{u}$ orbitals (Table I).

Since the calculation is numerical, i.e., it makes use of molecular diatomic orbitals expanded in partial waves expressed in spheroidal prolate coordinates [3] [thus avoiding expansion of the orbitals in (unknown) basis sets] it is often advantageous [4] to treat the initial guess directly as numerical one-electron diatomic molecular orbitals (OEDMO) rather than as a linear combination of atomic orbitals [3], because then the character of each orbital can be directly controlled. In the present work the use of OEDMO's as an initial guess to the SCF calculation [3] has been adopted either for all orbitals or, at


FIG. 1. The self-consistent (SCF) orbitals involved in the $\mathrm{He}_{2}{ }^{3} \Delta_{u}$ states of the present work (without nodes) and of Ref. [2] (with one node), represented by the points, compared with corresponding one-electron diatomic molecular orbitals (OEDMO), represented by the lines. The $\xi$ variable is $\xi=\left(r_{a}+r_{b}\right) / R_{a b}$, where $r_{a}$ and $r_{b}$ are the distances of the electron from the two nuclei $a$ and $b$, and $R_{a b}$ is the internuclear distance $\left(R_{a b}=2\right.$ a.u.). $\quad X_{1}(\xi)$ (represented by points) is the first (and main) term in a par-tial-wave expansion [3] of the SCF orbital wave function $\Psi_{\mathrm{SCF}}(\xi, \eta, \phi)=\Sigma_{l m} X_{l}(\xi) Y_{l m}(\eta, \phi)$, where $\eta=\left(r_{a}-r_{b}\right) / R_{a b}$, $\phi$ is the azimuthal angle of the electron position, and $Y_{l m}$ are spherical harmonics. The solid and dashed curves represent, respectively, the OEDMO's $1 \delta_{g}$ and $2 \delta_{g}$ [defined by ( $n l m$ ) united-atom quantum numbers (322) and (422), respectively] computed [4] with effective nuclear charges $z_{a}^{*}=z_{b}^{*}=0.5$ a.u. $\Xi(\xi)$ (represented by lines) is the radial-like part of the OEDMO wave function $\Psi_{\text {OEDMO }}(\xi, \eta, \phi)=\Xi(\xi) H(\eta) e^{i m \phi}$. The figure suggests that the SCF $\delta_{g}$ of the present work is practically $1 \delta_{g}$, whereas that of Ref. [2] is the $2 \delta_{g}$.

TABLE I. Three neutral $\mathrm{He}_{2}$ states as reported in Ref. [2]. Typical values of the total Hartree-Fock (HF) energy, the orbital energies, and the squared distance of the outer electron from the center of the molecule, at the equilibrium interatomic separation of 2 a.u. For the ${ }^{3} \Delta_{u}$ state the corresponding values from the present work are also displayed. (All quantities in a.u.)

| State | Outer orbital | $E_{\mathrm{HF}}$ | $\varepsilon\left(1 \sigma_{g}\right)$ | $\varepsilon\left(1 \sigma_{u}\right)$ | $\varepsilon_{\text {outer }}$ | $\left\langle R^{2}\right\rangle_{\text {outer }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| ${ }^{3} \Pi_{g}$ | $1 \pi_{u}$ | -5.051 | -1.42 | -1.21 | -0.13 | 27.5 |
| ${ }^{3} \Delta_{u}$ | $1 \delta_{g}$ | -4.954 | -1.61 | -1.40 | -0.03 | 515.3 |
|  | $1 \delta_{g}{ }^{a}$ | -4.978 | -1.57 | -1.35 | -0.05 | 130.2 |
| ${ }^{3} \Phi_{g}$ | $1 \phi_{u}$ | -4.954 | -1.61 | -1.40 | -0.03 | 364.4 |

${ }^{\text {a }}$ This work.
least, for the most diffuse ones.
In this paper it is shown that whereas some starting choices of the $\delta_{g}$ orbital lead to the results of Ref. [2], some other special choices may lead to lower energy. By using as an initial choice the $1 \delta_{g}$ OEDMO, defined by the united-atom quantum numbers (UAQN) $(n l m)=$ (322), with the appropriate nuclear charge screening, it is possible to achieve convergence for the state $\mathrm{He}_{2}{ }^{3} \Delta_{u}$ to energy values (Table II) which are lower than those reported in Ref. [2] by about 0.02 a.u. at all internuclear separations, and which indeed lie between those of $\mathrm{He}_{2}{ }^{3} \Pi_{g}$ and $\mathrm{He}_{2}{ }^{3} \Phi_{g}$. On the other hand, the choice of the $2 \delta_{g}$ OEDMO [with UAQN $(n l m)=(422)$ ] as an initial guess with a variety of nuclear charge screenings, leads to the [higher] SCF values reported in Ref. [2], or even higher. It should be noted that the choice of the $1 \delta_{g}$ OEDMO as an initial guess does not by itself guarantee convergence to the lower-lying state; it is essential to use appropriate nuclear charge screening, otherwise $1 \delta_{g}$ leads again to higher SCF values, either those of Ref. [2] or even higher. The difficulty encountered at determining the SCF lower energy of the $\mathrm{He}_{2}{ }^{3} \Delta_{u}$ state within the Hartree-Fock iterative scheme suggests that this state is, in the language of nonlinear phenomena, an attractor whose basin of attraction has a more limited extent than the higher-energy state of Ref. [2], and that other higher-
lying states are accessible from a much wider variety of initial conditions.

The character of the SCF $\delta_{g}$ orbitals involved in the lower $\mathrm{He}_{2}{ }^{3} \Delta_{u}$ state, reported here, and the higher one of Ref. [2], is shown in Fig. 1, for $R_{a b}=2$ a.u. The orbital of Ref. [2] has one node and thus corresponds to the $2 \delta_{g}$ whereas the present one has no nodes and corresponds to the $1 \delta_{g}$. For comparison, the pure OEDMO's $1 \delta_{g}$ and $2 \delta_{g}$ [defined by ( $n l m$ ) UAQNs (322) and (422), respectively] computed [4] with effective nuclear charges $z_{a}^{*}=z_{b}^{*}=0.5$ a.u. are also displayed. They are practically identical with the corresponding SCF orbitals of the two $\mathrm{He}_{2}{ }^{3} \Delta_{u}$ states in question. Furthermore, the squared distance $\left\langle R^{2}\right\rangle$ for these two OEDMO's equals 130.4 and 515.7 a.u., respectively, in remarkable agreement with the SCF values at $R_{a b}=2$ a.u.. Hence one can conclude that the Hartree-Fock configuration of the lower $\mathrm{He}_{2}{ }^{3} \Delta_{u}$ state is $\left(1 \sigma_{g}^{2} 1 \sigma_{u} 1 \delta_{g}\right)$ whereas that of the higher one (reported in Ref. [2]) is ( $1 \sigma_{g}^{2} 1 \sigma_{u} 2 \delta_{g}$ ).

A similar treatment of the $\mathrm{He}_{2}{ }^{3} \Pi_{g}$ and $\mathrm{He}_{2}{ }^{3} \Phi_{g}$ states as well as the $\mathrm{He}_{2}-{ }^{4} \Phi_{g}$ and $\mathrm{He}_{2}-{ }^{4} I_{g}$ states did not reveal any other attractor than those reported in Ref. [2].

As a corollary there should be a reassessment of the question of the boundedness of the $\mathrm{He}_{2}-{ }^{4} I_{g}$ metastable

TABLE II. Total Hartree-Fock (HF) energies, occupied orbital energies, and expectation values of $\left\langle R^{2}\right\rangle$ of the $1 \delta_{g}$ orbital (all in a.u.) for the $\mathrm{He}_{2}{ }^{3} \Delta_{u}:\left(1 \sigma_{g}^{2} 1 \sigma_{u} 1 \delta_{g}\right)$ state as a function of the internuclear separation $R_{a b}$.

| $R_{a b}$ | $E_{\mathrm{HF}}$ | $\varepsilon\left(1 \sigma_{g}\right)$ | $\varepsilon\left(1 \sigma_{u}\right)$ | $\varepsilon\left(1 \delta_{g}\right)$ | $\left\langle R^{2}\right\rangle\left(1 \delta_{g}\right)$ |
| :--- | :---: | :---: | :---: | :---: | :---: |
| 0.5 | -2.575887 | -3.39631 | -0.50136 | -0.057073 | 117.6 |
| 0.7 | -3.841682 | -2.85017 | -0.62026 | -0.056406 | 121.2 |
| 1.0 | -4.562558 | -2.29011 | -0.86277 | -0.055788 | 124.6 |
| 1.4 | -4.888717 | -1.87757 | -1.13702 | -0.055229 | 127.2 |
| 1.6 | -4.946615 | -1.74735 | -1.23034 | -0.055140 | 128.2 |
| 1.8 | -4.971656 | -1.64667 | -1.29918 | -0.054961 | 129.2 |
| 2.0 | -4.977913 | -1.56714 | -1.34896 | -0.054787 | 130.2 |
| 2.2 | -4.973931 | -1.50328 | -1.38437 | -0.054614 | 131.2 |
| 2.4 | -4.964874 | -1.45133 | -1.40907 | -0.054444 | 132.2 |
| 2.6 | -4.953807 | -1.40862 | -1.42583 | -0.054274 | 133.1 |
| 3.0 | -4.931858 | -1.34354 | -1.44337 | -0.053933 | 135.1 |
| 4.0 | -4.896782 | -1.25064 | -1.44440 | -0.053034 | 140.5 |
| 5.0 | -4.883651 | -1.20575 | -1.43069 | -0.052025 | 146.9 |
| 6.0 | -4.878938 | -1.18107 | -1.41887 | -0.050921 | 154.2 |
| 7.0 | -4.876754 | -1.16587 | -1.41069 | -0.049765 | 162.4 |

TABLE III. Total Hartree-Fock (HF) energies (in a.u.) of the $\mathrm{He}_{2}{ }^{3} \Pi_{g},{ }^{3} \Delta_{u}$, and ${ }^{3} \Phi_{g}$ and the $\mathrm{He}_{2}-{ }^{4} \Phi_{g}$ and ${ }^{4} I_{g}$ states at $R_{a b}=2$ a.u.

| $\mathrm{He}_{2}$ state | $E_{\mathrm{HF}}$ | $\mathrm{He}_{2}-$ state | $E_{\mathrm{HF}}$ |
| :---: | :---: | :---: | :---: |
| ${ }^{3} \Pi_{g}:\left(1 \sigma_{g}^{2} 1 \sigma_{u} 1 \pi_{u}\right)$ | -5.0512 | ${ }^{4} \Phi_{g}:\left(1 \sigma_{g}^{2} 1 \sigma_{u} 1 \pi_{u} 1 \delta_{g}\right)$ | -4.9818 |
| ${ }^{3} \Delta_{u}:\left(1 \sigma_{g}^{2} 1 \sigma_{u} 1 \delta_{g}\right)$ | -4.9779 | ${ }^{4} I_{g}:\left(1 \sigma_{g}^{2} 1 \sigma_{u} 1 \delta_{g} 1 \phi_{u}\right)$ | -4.9544 |
| ${ }^{3} \Phi_{g}:\left(1 \sigma_{g}^{2} 1 \sigma_{u} 1 \phi_{u}\right)$ | -4.9542 |  |  |

state [2]. The results presented in Table III (for $R_{a b}=2$ a.u.) suggest that both ionic $\mathrm{He}_{2}-{ }^{4} \Phi_{g}$ and $\mathrm{He}_{2}-{ }^{4} I_{g}$ metastable states are unbound with respect to one of their neutral parent states.

Professor E.A. McCullough, who has kindly provided our institute with the program PWMCSCF, is gratefully acknowledged.
[1] Y.K. Bae, M.J. Coggiola, and J.R. Peterson, Phys. Rev. Lett. 52, 747 (1984); T.J. Klave, R.N. Compton, G.D. Alton, J.S. Thompson, and D.J. Pegg, Phys. Rev. Lett. 56, 582 (1986).
[2] L. Adamowicz and T. Pluta, Chem. Phys. Lett. 179, 517 (1991).
[3] L. Adamowicz and E.A. McCullough, Jr., J. Chem. Phys. 75, 2475 (1981); E.A. McCullough, Jr., Comput. Phys. Rep. 4, 267 (1986); Chem. Phys. Lett. 24, 55 (1974); J. Chem. Phys. 62, 3991 (1975).
[4] N.C. Bacalis, Y. Komninos and Cl. A. Nicolaides, Phys. Rev. A 45, 2701 (1992).

