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Determination of highly excited states of diatomic-molecular ions using exact $H_2{}^+$-like orbitals

C. Le Sech
Laboratoire des Collisions Atomiques et Moléculaires (Unité Associée au CNRS No. 281), Université de Paris-Sud, Bâtiment 351, 91405 Orsay Cedex, France

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A simple configuration-interaction method to calculate accurate electronic energies of two-electron molecular ions at intermediate internuclear distances is presented. The correlated basis functions are constructed from exact $H_2{}^+$ molecular orbitals, and include an explicit dependence on the interelectronic distance in order to describe the cusp conditions of the Coulombic field. An important simplification of the Hamiltonian matrix elements is deduced. The method is applied to determine new potential curves of highly excited states of $He_2{}^{2+}$ molecular ions dissociating into two excited fragments. The ${}^1\Sigma_g$ state dissociating into $He^+(2p)+He^+(2p)$ presents a deep well located at $R=5.0$ a.u., where metastable states can survive. These states could be of interest in excimer lasers.

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The determination of accurate potential curves of diatomic molecular ions at intermediate and large internuclear distances—typically more than 4 a.u.—is important and remains an open problem in chemical physics. It is known that only the simplest system, $H_2{}^+$, can be studied exactly, within the Born-Oppenheimer approximation. This follows from the separability of the Schrödinger equation in prolate spheroidal coordinates [1]. Much work has been devoted to this model system in order to understand which are the important parameters governing the fine balance between electronic exchange and electronic polarization. They ultimately explain the intermediate and long-range interactions of this ion. Recent works of Scott, Dalgarno, and Morgan, and references therein, illustrate these problems [2]. It is shown that it is crucial to describe carefully the electronic polarization due to the nuclei at the first step of the theoretical treatment in order to reproduce correctly the electronic exchange at intermediate and large distances, even for the ground state of this ion.

The study of multielectron molecular ions is of interest. The $He_2{}^{2+}$ molecular ion has a well in its potential curve for the ground state, allowing trapped metastable states. It is tempting to study highly excited states; for example, those dissociating into two excited atoms, in order to see if some electronic potential curves have a well by which excited states are allowed to survive. One can speculate that these states could be of interest in building excimer lasers with a wavelength in the far uv range. To the best of our knowledge, only a very few studies of these states have been made before (see below).

This problem is not easy. It is of major importance in studying excited states to include the electronic polarization carefully from the beginning. We have in addition the difficult task of describing the Coulombic interaction between the electrons. The orbitals studied by Scott, Dalgarno, and Morgan [2] include the true polarization, but it seems difficult to introduce the interelectronic correlation within this approach. Also the determination of excited orbitals and the treatment of their degeneracies are far from straightforward. The usual methods of quantum chemistry are not well suited at first sight. They neither take into account the correct polarization nor do they treat the important cusp conditions and Kato's theorem [4] in a convenient way. To obtain reliable results, it is necessary to perform a large configuration interaction (CI), or to optimize many variational parameters in a sophisticated wave function in a James-Coolidge approach. Indeed relatively few molecular ions have been studied with these methods. Results are only available for the first excited states, and are restricted more or less to internuclear distances of the covalent range.

Following a different approach, exact $H_2{}^+$ orbitals are attractive as a starting point to study multielectron molecular ions [5] ($H_2{}^+$ orbitals mean here more generally the exact solutions of the two-center Coulombic field problem with charges Z_A,Z_B located at points A,B separated by the distance R: "$H_2{}^+$-like" orbitals [6]). Indeed this choice includes in a natural way the *electronic polarization* due to the nuclei. Unfortunately they look to be inappropriate to describe molecular ions beyond $H_2{}^+$ at intermediate and large internuclear separations, due to the well-known problem of an incorrect atomic dissociation limit [7].

In the present work we want to show that the $H_2{}^+$-like orbitals remain good candidates for describing the behavior of molecular-ion potentials at intermediate and long-range internuclear distances. The key to our approach lies in a *simple and accurate* description of the electronic correlation in order to restore the correct dissociation limit. To do so we proceed in two steps. First, we introduce explicitly the interelectronic distance r_{12} in the molecular wave function of the ion, built with $H_2{}^+$ orbitals; second, we perform a *small* CI between these correlated basis states.

We derive an expression for the Hamiltonian matrix elements between functions written as the product $\Psi_i=\Phi_1\Omega$, $\Psi_j=\Phi_j\Omega$. The result is quite general and will be very useful in performing the CI. Setting the Laplacian $\vec{\nabla}_6^2=\vec{\nabla}_1^2+\vec{\nabla}_2^2$ and the gradient $\vec{\nabla}_6=\vec{\nabla}_1+\vec{\nabla}_2$, where the indices 1, 2, and 6 stand for the three coordinates of electrons 1, 2, and all the (six) coordinates, respectively. The Hamiltonian operator H is written in the nonrelativistic approximation, using atomic units:

$$H=-\vec{\nabla}_6^2/2+V_1+V_2+1/r_{12},$$

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where V_k is the potential acting upon electron $k=1,2$. The matrix elements H_{ij} are given by the expression

$$H_{ij}=\langle\Phi_i\Omega|-\vec{\nabla}_6^2/2+V_1+V_2+1/r_{12}|\Phi_j\Omega\rangle$$
$$=\left\langle -\Omega^2\Phi_i\frac{\vec{\nabla}_6^2\Phi_j}{2}-\Phi_j\Phi_i\Omega\,\frac{\vec{\nabla}_6^2\Omega}{2}-\Phi_i\Omega\vec{\nabla}_6\Phi_j\cdot\vec{\nabla}_6\Omega\right.$$
$$\left.+\Phi_i\Omega(V_1+V_2+1/r_{12})\Phi_j\Omega\right\rangle.$$

The strategy is to remove the term $I=\langle\Phi_i\Omega\vec{\nabla}_6\Phi_j\cdot\vec{\nabla}_6\Omega\rangle$ in the above expression, as it involves a difficult integration on all the space coordinates. To do so we rewrite I as

$$I=\tfrac{1}{4}\int[\vec{\nabla}_6(\Phi_i\Phi_j)+\Phi_i\vec{\nabla}_6\Phi_j-\Phi_j\vec{\nabla}_6\Phi_i]\cdot\vec{\nabla}_6\Omega^2 d\tau$$

and twice perform integrations by part (first Green transformation). Taking into account the relation $\vec{\nabla}_6^2\Omega^2=2\Omega\vec{\nabla}_6^2\Omega+2\vec{\nabla}_6\Omega\cdot\vec{\nabla}_6\Omega$ results in the cancellation of some terms. Finally we find

$$H_{ij}=\left\langle\Phi_i\Phi_j\frac{\vec{\nabla}_6\Omega\cdot\vec{\nabla}_6\Omega}{2}-\frac{\Omega^2}{4}[\Phi_i\vec{\nabla}_6^2\Phi_j+\Phi_j\vec{\nabla}_6^2\Phi_i]\right.$$
$$\left.+(V_1+V_2+1/r_{12})\Phi_i\Phi_j\Omega^2\right\rangle.$$

Up to this point no particular choice is made for Φ and Ω. The net gain in the above formula is that we now have the term $\vec{\nabla}_6\Omega\cdot\vec{\nabla}_6\Omega$ instead of $\vec{\nabla}_6\Phi_j\cdot\vec{\nabla}_6\Omega$. We shall see below that Ω can be chosen quite generally as an analytical form leading to a convenient expression for the dot product $\vec{\nabla}_6\Omega\cdot\vec{\nabla}_6\Omega$. Now we specify the function $\Psi=\Phi\Omega$. Let the function Φ stand for the electronic configuration, built on $H_2{}^+$-like orbitals. Explicitly we take for Φ an antisymmetrized function $\Phi=A(\phi_n\phi_{n'})$, ϕ_n being the $H_2{}^+$ orbital's exact solution of

$$(-\vec{\nabla}_k^2/2+V_k)\phi_n=\varepsilon_n\phi_n,\quad V_k=-Z_A/r_{kA}-Z_B/r_{kB},\quad k=1,2.$$

In this equation Z_A,Z_B are the nuclear charges, located at points A and B with separation R; r_{kA},r_{kB} are the distances of the electron k to A,B, respectively; and ε_n is the electronic energy of $H_2{}^+$ at this internuclear distance. The configuration wave function Φ_i is the solution of

$(-\vec{\nabla}^2{}_6/2+V_1+V_2)\Phi=E_i\Phi$ with eigenvalue $E_i=\varepsilon_n+\varepsilon_{n'}$.

As an example, the ground-state configuration ϕ_1 is (with the usual united-atom notation)

$$\Phi_1=\phi_{1s\sigma}(1)\phi_{1s\sigma}(2)[\alpha(1)\beta(2)-\alpha(2)\beta(1)]/\sqrt{2}.$$

The electronic spins are described by the function $[\alpha(1)\beta(2)-\alpha(2)\beta(1)]/\sqrt{2}$ and need not be considered explicitly.

The function Ω is chosen in order to take into account the major part of the interelectronic correlation due to the Coulomb repulsion. The simplest choice follows Hylleraas [8]: $\Omega(r_{12})=1+0.5r_{12}$. A more involved functional form for $\Omega(r_{12})$ could be chosen; some examples can be found in a recent study of neutral diatomic molecules [9]. But it was not necessary here to do that, as the description of the correlation will be enhanced subsequently by performing a small CI between these correlated basis functions.

The present definitions of Φ and Ω take into account not only the electronic polarization, but also insure the fulfillment of the important cusp conditions of the molecular wave function [4]. This specific choice of Φ and Ω leads to further important simplifications. Finally the Hamiltonian matrix elements can be written in a very simple form:

$$H_{ij}=\langle\Phi_i\Phi_j\Omega^2[1/r_{12}+(E_i+E_j)/2]\rangle,$$

reducing the present calculations *involving explicitly correlated wave functions* to the familiar computations of quantum chemistry using well-known bielectronic integrals.

In the past, interesting attempts have been made by Conroy to obtain solutions for molecular few-electron problems also incorporating exact cusp conditions [10], and by Wilets, Henley, and Martensson [11]. In these references, an important feature, in common with the present work, is the factorization of the full wave function as a product $\Psi=SC$, where S is called the "shape function" and is related to the orbital part, and C is an analytical function describing the correlation of the electrons (here we have written $\Psi=\Phi\Omega$). Results for molecular systems containing up to four electrons have been presented for the ground states. This suggests that the extension of our approach to few-electron systems could be feasible in principle. The simplification of the matrix elements that we have deduced above via the Green transformation could be valuable in practical calculations on these few-electron systems. Basically it involves only the factorization of the full wave function, which remains possible, as shown by Conroy; see also a discussion on the Jastrow factor in Wilets's paper.

An alternative way to extend the method to multielectron systems is the introduction of an effective potential that affects a special electron in a molecule. Following this rationale, we have already performed studies of alkali-metal dimers like Na_2, but have restricted them to a single-configuration wave function in the covalent range [12]. No doubt that the present work will improve this previous approach for future work.

To check the accuracy of the present method we have calculated the ground-state energy of the $He_2{}^{2+}$ molecular ion. For this system very accurate calculations exist up to $R=4.5$ a.u. made by Yagisawa, Sato, and Watanabe [13], using sophisticated James and Coolidge wave functions. For larger internuclear distances, accurate determinations of the potential curve were performed by Sato and Hara [14] and Cohen and Bardsley [15], using respectively the full CI method—introducing typically 100 configurations—and the generalized valence-bond method. The first excited states ${}^1\Sigma_g$ and ${}^1\Sigma_u$ have also been calculated with great accuracy by Bishop and Cheung [16]. The potential curve of the lowest state has a well-known dip, and is the reason why long-

TABLE I. Electronic energies (a.u.) as a function of R for the $X\,^1\Sigma_g$ state of $He_2{}^{2+}$, including the nuclear repulsion $4/R$, determined using different approaches (see text).

R (a.u.)	Present results	Results from Ref. [13]	Results from Ref. [14]	Results from Ref. [15]
0.5	-1.9298	-1.9486	-1.9405	
1.0	-3.5840	-3.5997	-3.5909	$-3.597\,02$
1.5	-3.6590	-3.6725	-3.6645	$-3.670\,62$
2.0	-3.6225	-3.6302	-3.6253	$-3.629\,37$
2.5	-3.6345	-3.6370		$-3.637\,29$
3.0	-3.6750	-3.6755	-3.6724	$-3.676\,74$
3.5	-3.7172	-3.7118	-3.7130	$-3.717\,55$
4.0	-3.7516	-3.7399	-3.7470	$-3.751\,41$
4.5	-3.7790	-3.7573	-3.7743	$-3.778\,54$
5.0	-3.8017		-3.7970	$-3.800\,48$
6.0	-3.8345			$-3.833\,55$
7.0	-3.8579			
8.0	-3.8753			$-3.875\,07$
9.0	-3.8886			
10.0	-3.8990		-3.8965	$-3.900\,03$

lived metastable states can exist ($D_e = 1.6$ eV). More recently this state has been studied by Nicolaides [3], who speculates on the interest in the ability of the trapped metastable states in the ground state to store energy.

Table I reports the present results obtained for the ground $^1\Sigma_g$ state, calculated with *only a two-configuration-state wave function, without any variational parameter*: $\Psi_i = [c_1\Phi(1s\sigma^2) + c_2\Phi(2p\sigma^2)]\Omega$. They are compared with the best values available from the authors quoted above. One can notice that for internuclear distances $R < 3.0$ a.u., our results are slightly above those of Yagisawa, Sato, and Watanabe [13] and Sato and Hara [14], but for $R > 3$ a.u. our values lie *below*, and lead to the expected $1/R$ behavior at larger distances. In the range 3.5 a.u.$<R<$8.0 a.u. our values are also below those obtained by Cohen and Bardsley [15], which are the best results for large distances. The slight apparent discrepancy occurring for $R = 10.0$ a.u.—our result is $E = -3.8990$ a.u. instead of -3.90003 a.u. given by Cohen *et al.*—is not due to our method itself, but has to be attributed to the present numerical accuracy for integrations, which degrades a little as R increases beyond, typically, 8.0 a.u. for low-lying states, especially for the ground state. The reason is related to the fact that for *large values of* R, exact molecular orbitals behave like very rapidly decreasing exponential functions in order to reproduce the nearly atomic behavior of the electrons on each nucleus. We have checked that the present numerical accuracy is equal to or is better than 0.001 a.u. for the ground state and 0.0001 a.u. for the excited states, which are discussed below, for all internuclear distances. The numerical accuracy can be improved by using more points in the Gauss-Legendre integration than has been done in the present work—we have taken at most only 16 Gaussian points for each quadrature in the present work—or taking the more suitable Gauss-Laguerre integration for large values of R, if greater accuracy is really needed.

The previous discussion demonstrates the validity of our approach, and proves clearly the benefit of introducing from the very beginning the theoretical expression for the correct electronic polarization and the cusp conditions. In the usual approaches (CI, or variational methods) many parameters or configurations are necessary to reproduce the electronic polarizability and the regular singularities of the Coulombic field, resulting in a less efficient approach, especially at intermediate and large internuclear distances. This is particularly true for excited states of molecules bearing electric charges where polarization is of the greatest importance. Finally let us note that taking exactly into account the molecular-orbital polarization ensures the correct description of the Stark effect of the hydrogenoid ion $He^+(n=2)$ in the electric field of the other ion at large internuclear separations. We have calculated several other excited states, and could draw for them similar conclusions; thus we do not report these results here, as they are already accurately known.

TABLE II. Comparison of the electronic energies (a.u.) for different internuclear distances R for the $^1\Sigma_g$ states of $He_2{}^{2+}$ dissociating the $He^+(2p)+He^+(2p)$ state (1) and the $He^+(2s)+He^+(2p)$ state (2), including $4/R$, with the results of Sato and Hara [14] (see text).

R(a.u.)	State (1) Present results	$1\,^1\Sigma_g[AI(1\sigma_g,1\sigma_u)]$ Sato and Hara [14]	State (2) Present results	$2\,^1\Sigma_g[AI(1\sigma_g,1\sigma_u)]$ Sato and Hara [14]
3.0	-0.7090	-0.7313	-0.6057	-0.6086
3.5	-0.8740	-0.8709	-0.7418	-0.7251
4.0	-0.9540	-0.9467	-0.8189	-0.7994
4.5	-0.9871	-0.9793		-0.8434
5.0	-0.9940	-0.9879	-0.8805	-0.8673
10.0	-0.9267	-0.9284	-0.9101	-0.9086

Furthermore we have been motivated to apply our method to determine highly excited states. It is tempting to study those states dissociating into $He^+(n=2)+He^+(n=2)$. They appear to be of interest if their behavior can be found to be similar to that of the ground state. We have considered the molecular configurations $(2s\sigma_g)^2$, $(3p\sigma_u)^2$, $(3d\sigma_g)^2$, and $(4f\sigma_u)^2$, all $^1\Sigma_g$ states dissociating into $He^+(n=2)$. To the best of our knowledge, few calculations exist on such highly excited states. Sato and Hara [14] have studied some of these states, which they denote as $1\,^1\Sigma_g[AI(1\sigma_g,1\sigma_u)]$ and $2\,^1\Sigma_g[AI(1\sigma_g,1\sigma_u)]$. Comparing our values for the states dissociating into $He^+(2p_0)+He^+(2p_0)$ and $He^+(2s)+He^+(2p_0)$, we have been able to assign the former to the $1\,^1\Sigma_g[AI(1\sigma_g,1\sigma_u)]$ and the latter to the $2\,^1\Sigma_g[AI(1\sigma_g,1\sigma_u)]$. We compare in Table II the numerical values obtained by our method to those calculated by Sato and Hara [14] for these two states. One can check that all the energy values are close to each other for different internuclear distances. As an example, for $R=5.0$ a.u. the energy's values differ by 6×10^{-3} a.u. The previous authors did not notice the well in the state dissociating into $He^+(2p_0)+He^+(2p_0)$ that we present below, as they did not take into account the $4/R$ repulsion term. Let us remember that the present wave function is compact and simple, and could be useful for further calculations on the dynamical properties of these states.

We display in Figs. 1 and 2 the electronic energy values of the states dissociating $He^+(2p_0)+He^+(2p_0)$, $He^+(2s)+He^+(2p_0)$, $He^+(2s)+He^+(2s)$, and $He^+(2p)+He^+(3p)$. One can notice that the state dissociating $He^+(2p_0)+He^+(2p_0)$, which is a mixture of covalent and ionic states $(3d\sigma_g)^2$, $(4f\sigma_u)^2$, has a potential well at $R=5.0$ a.u., of

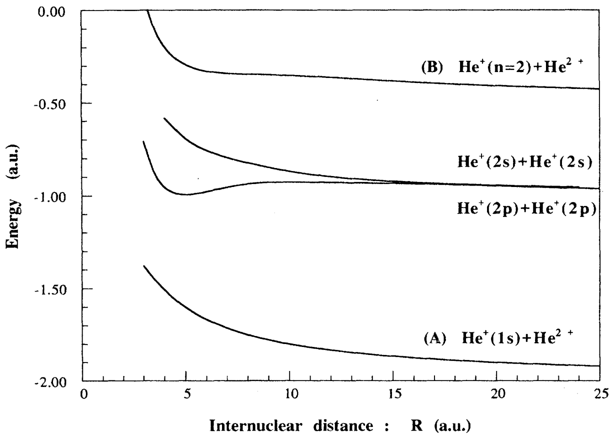

FIG. 1. The two lowest energies of the molecular configurations: $(2s\sigma_g)^2$, $(3p\sigma_u)^2$, $(3d\sigma_g)^2$, and $(4f\sigma_u)^2$, all ${}^1\Sigma_g$ states of ${\rm He_2}^{2+}$ dissociating into $\mathrm{He}^+(n=2)$. Curves A and B represent the thresholds of two continua corresponding to $\mathrm{He}^+(1s)+\mathrm{He}^{2+}+e$ and $\mathrm{He}^+(2s;2p)+\mathrm{He}^{2+}+e$ states.

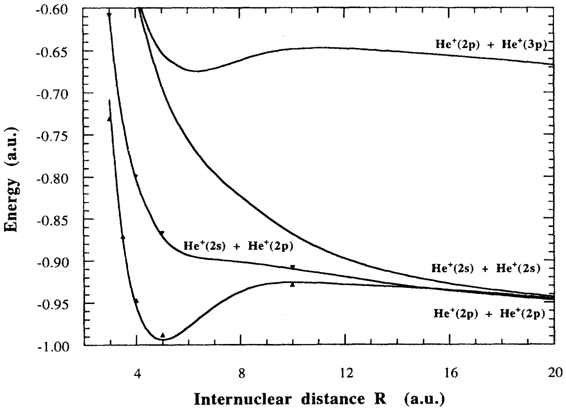

FIG. 2. Details of the potential well of the ${}^1\Sigma_g$ states dissociating into $\mathrm{He}^+(2p_0)+\mathrm{He}^+(2p_0)$ and $\mathrm{He}^+(2p_0)+\mathrm{He}^+(3p_0)$, located respectively at $R=5$ and 6 a.u. Full triangles, values of the states $1\,{}^1\Sigma_g[AI(1\sigma_g,1\sigma_u)]$ and $2\,{}^1\Sigma_g[AI(1\sigma_g,1\sigma_u)]$ taken from Sato and Hara [14] adding $4/R$.

depth $D_e=1.84$ eV. Figure 2 is an enlargement of the well of the state dissociating into $\mathrm{He}^+(2p_0)+\mathrm{He}^+(2p_0)$. The full triangles are the values taken from Sato and Hara [14] for corresponding states. We also show the well occurring at $R=6.0$ a.u. with depth $D_e'=0.72$ eV for the ${}^1\Sigma_g$ state dissociating $\mathrm{He}^+(2p_0)+\mathrm{He}^+(3p_0)$. It has been determined in a similar way. The height of the barrier of the state dissociating $\mathrm{He}^+(2p_0)+\mathrm{He}^+(2p_0)D_e=1.84$ eV precludes the decay by rapid tunneling. As this state is well separated from the $\mathrm{He}^+(1s)+\mathrm{He}^{2+}+e$ and $\mathrm{He}^+(2s;2p)+\mathrm{He}^{2+}+e$ continua—and assuming it can be populated—this excimer state could be a good candidate for decaying significantly via *radiative transitions* to the repulsive ungerade states that are necessarily below the $\mathrm{He}^+(1s)+\mathrm{He}^{2+}$ limit, typically emitting photons of 30 eV.

In the present work we have shown that it is important to include in the wave function the correct electronic polarization and cusp conditions in order to describe in a simple and efficient way the molecular ions at intermediate internuclear distances. A convenient description of the interelectronic interactions can restore the correct atomic-state dissociation limits. Highly excited states, where polarization becomes very crucial, can be studied easily following this approach. We have illustrated this point by calculating states dissociating into two excited $\mathrm{He}^+(n=2)$ ions. The wave function that we have considered here is only a two-state wave function and contains no variational parameters. The validity of the present approach for studying highly excited states is confirmed by comparison with other theoretical determinations of such states. We observe that in the range of internuclear distances 3.0 a.u. $<R<8.0$ a.u. our energy value determination can be compared favorably to the best one presently available, even for the ground state. We have found that the ${}^1\Sigma_g$ state of the molecular ion ${\rm He_2}^{2+}$ dissociating into $\mathrm{He}^+(2p_0)+\mathrm{He}^+(2p_0)$ has a deep potential well located at 5.0 a.u., authorizing metastable states that could be of interest in excimer lasers.

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