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Stability of two-electron diatomic molecules

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Abstract

We present a detailed study of the ground state behaviour of two-electron diatomic molecules. The ground state stability diagram for diatomic molecules in the Born–Oppenheimer approximation is obtained and the behaviour of the ground state near the stability line is studied. Two different cases are analysed: the homonuclear two-centre two-electron molecule with the internuclear distance as a free parameter and the diatomic two-electron molecule (in this case, the internuclear distance is determined by equilibrium conditions). Analytical and numerical results for these systems are presented.

1. Introduction

The study of stability of bound states for atomic and molecular systems as a function of physical parameters, such as nuclear charges, nuclear distances, is a subject of great interest. Multiple charged anions could be unstable against ionization, and experimental and theoretical search of small stable multiple charged anions is an active research field [1]. On the other hand, in the case of highly ionized molecules, nuclear Coulombic repulsion turns these systems unstable against dissociation. However, even at the present time when we are able to make calculations for many body systems, like extremely large molecules, some properties of small molecules are still being a great subject of study. The ground state of simple molecules like the hydrogen molecule, the helium hydride molecular ion and the helium molecular dication was studied with a great detail [2–7]. In this work we study the ground state of two-electron diatomic molecules change as a function of the nuclear charges in the Born–Oppenheimer approximation. Our principal aim is to present the ground state stability diagram in the nuclear charge plane, and to elucidate how stability is lost.

Some aspects of the stability of two-electron homonuclear diatomic molecule ground state have been studied previously [8]. A complete stability diagram in the large-dimension limit approximation has also been presented [9, 10]. For a two-electron diatomic molecule, the binding characteristics are entirely determined by the nuclear charges involved. Given a stable configuration (like the hydrogen molecule) if we increase the nuclear charges, the system

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will turn into a quasi-stable state (metastability, caused by possible tunnelling dissociation through energy barriers) and if we keep increasing the nuclear charges, we finally arrive at a completely unstable situation. If we now decrease the nuclear charges, there must exist a point for which the system cannot bind two electrons, and then we arrive again at an unstable picture. Although the ground state properties of two-electron diatomic molecules have been widely studied, the critical behaviour of such systems is not completely understood.

Even a realistic situation arises when the internuclear distance is determined as the equilibrium distance for fixed values of nuclear charges; it is interesting to study the ground state as a function of all the parameters of the Hamiltonian treated as independent variables. In this case, we can apply a finite size scaling method [11–13] to analyse the properties of the system near the ionization threshold in the space of the Hamiltonian parameters.

Numerical calculations for the ground state energy were done using the Ritz variational method [14]. Hamiltonian matrix elements were calculated applying a recently developed method for the evaluation of two-centre two-electron integrals [15]. For values of the nuclear charge where numerical evaluations are particularly difficult [4], the variational results were corroborated with quantum diffusion Monte Carlo calculations for the ground state energy.

This paper is organized as follows. In section 2 we give a short review of the numerical treatment of the two-electron two-centre Hamiltonian. In section 3 we study the homonuclear two-electron system as a function of the Hamiltonian parameters as independent variables. We obtain the critical line and other interesting quantities that reveal the behaviour of the ground state energy near this line. In section 4 we work with homonuclear and heteronuclear diatomic molecules fixing the internuclear distance as the equilibrium distance. In this case we obtain a ground state stability diagram in the space of nuclear charges. More rigorous definitions will be established in sections 3 and 4. Finally, the conclusions are given in section 5.

2. The two-electron, two-centre system: numerical treatment

The two-centre two-electron electronic Hamiltonian, in atomic units, takes the form

$$H_e(R, Z_a, Z_b) = \sum_{i=1}^{2}\left(-\frac{1}{2}\nabla_i^2 - \frac{Z_a}{|\vec{r}_i - \vec{R}/2|} - \frac{Z_b}{|\vec{r}_i + \vec{R}/2|}\right) + \frac{1}{r_{12}}, \qquad (1)$$

where the nuclei with charges Z_a and Z_b are located in the z-axis at $R/2$ and $-R/2$, respectively, and r_{12} is the interelectronic distance.

In order to apply a variational approach, we used the trial wavefunction

$$\Psi(\vec{r}_1, \vec{r}_2; \vec{R}, Z_a, Z_b) = \sum_n a_n(\vec{R}, Z_a, Z_b)\Phi_n(\vec{r}_1, \vec{r}_2), \qquad (2)$$

where n represents the correspondent set of quantum numbers. The basis set $\{\Phi_n\}$ consists of functions of the type

$$\Phi_n = C\,\mathrm{e}^{-(\alpha\xi_1+\beta\xi_2)}\left(\xi_1^{p_n}\eta_1^{q_n}\xi_2^{r_n}\eta_2^{s_n} + \xi_1^{r_n}\eta_1^{s_n}\xi_2^{p_n}\eta_2^{q_n}\right) r_{12}^{m_n}; \qquad (3)$$

here, C is the normalization constant, (ξ, η, ϕ) [17] are usual prolate spheroidal coordinates, ϕ is the azimuthal angle, $\xi = (r_a + r_b)/R$, $\eta = (r_a - r_b)/R$, r_a and r_b are the distances to the centres and α and β are variational parameters. Powers are integer numbers with $p_n, q_n, r_n, s_n \geqslant 0$ and $m_n \geqslant -1$. This basis set has been used since the pioneering work of James and Coolidge [16].

In order to approximate the different quantities, we have to truncate the series, equation (2) at order $n = N$. Then the Hamiltonian is replaced by $M(N) \times M(N)$ matrix, with $M(N)$ being the number of elements in the truncated basis set at order N.

For $Z_a = Z_b$ it is obvious that the ground state wavefunction has to be invariant under inversion with respect to the plane of symmetry of the molecule. As a result, we have the restriction that $q_n + s_n$ must be even. In the heteronuclear case, we must consider all the basis functions with no restriction over $q_n + s_n$. In order to apply the Ritz variational method to evaluate the ground state energy, we have to solve the generalized eigenvalue problem

$$\det(H - \lambda S) = 0, \tag{4}$$

where λ is an eigenvalue, and the matrix elements are given by

$$H_{ij} = \langle \Phi_i | H_e | \Phi_j \rangle \qquad S_{ij} = \langle \Phi_i | \Phi_j \rangle. \tag{5}$$

The lowest eigenvalue of equation (4) is a variational upper bound to the ground state energy [14]. The generalized eigenvalue problem (4) is transformed to an usual symmetric eigenvalue problem by using a Cholesky decomposition for the overlap matrix S [18]

$$\det(\tilde{H} - \lambda I) = 0, \qquad \tilde{H} = L^{-1} H (L^{-1})^{\dagger}, \qquad LL^{\dagger} = S. \tag{6}$$

The basic integrals that appear in a two-electron two-centre James–Coolidge [16] ground state expansion of the diatomic two-electron system are of the form [2]

$$I^m_{pqrs} = \int d^3x_1 d^3x_2 \frac{\mathrm{e}^{-(\alpha\xi_1 + \beta\xi_2)}}{\xi_1^2 - \eta_1^2} \xi_1^p \eta_1^q \xi_2^r \eta_2^s r_{12}^m. \tag{7}$$

In a recent work [15] we developed an efficient method to evaluate these integrals. All the integrals needed for the evaluation of the matrix elements are obtained as analytic recursion expressions. In order to obtain the transformed matrix $\tilde{H}$ correct up to 16 decimal places, we used multi-precision Fortran [19], an extension of standard Fortran 90 that allows us to work with an arbitrary number of a significant figure. Once the matrix $\tilde{H}$ is obtained, the eigenvalue problem in equation (6) is solved using a standard double precision Fortran code.

It is well known that elliptic coordinates are best suited for intermediate values of the product ZR [4] and symmetric systems. In this work we are interested in a wide region of internuclear distances and in very asymmetric systems. In order to check the results in some regions of the Hamiltonian parameters, we develop a simple diffusion quantum Monte Carlo (DQMC) [20, 21] code. We construct DQMC with importance sampling using

$$\Phi(\mathbf{R}) = f(r_{12}) g(\vec{r}_1) g(\vec{r}_2) \tag{8}$$

as the guiding function, where $f(r)$ is the two-body Jastrow correlation factor

$$f(r) = \exp\left[\frac{r}{2(1 + \beta r)}\right], \tag{9}$$

and the single particle function $g(\vec{r})$ is

$$g(\vec{r}) = \mathrm{e}^{-\alpha_a r_a} + \mathrm{e}^{-\alpha_b r_b}. \tag{10}$$

The parameters α_a and α_b are determined in order to fulfil the cusp condition, and β is a variational parameter calculated in a simple variational Monte Carlo simulation (VMC) [20].

Even when DQMC results are not as accurate as variational calculations, this method can ensure the same accuracy in all the Hamiltonian parameter region. This allows us to check the validity of the variational calculations in the regions mentioned before.

3. Near-threshold behaviour of the two-electron, two-centre homonuclear system

In this section we study the near-threshold properties of a two-electron two-centre homonuclear Hamiltonian for small values of the nuclear charges, near the ionization threshold. We therefore take $Z_a = Z_b = Z$ in the Hamiltonian (1). For a fixed value of R, we find the value of the parameter Z ($Z_c(R)$) such that the energy of the two-electron system becomes degenerate with the threshold energy, the one-electron two-centre ground state energy.

The critical behaviour for $R \gg 1$ can be obtained analytically. A first-order perturbation calculation [14] gives

$$E_{0p}^{\mathrm{H}_2} = -Z^2 + \frac{Z^2}{R} + \frac{1}{R} - \frac{2Z}{R} \tag{11}$$

$$E_{0p}^{\mathrm{H}_2^+} = -\frac{Z^2}{2} + \frac{Z^2}{R} - \frac{Z}{R}, \tag{12}$$

where equation (11) is the first-order perturbation expansion for the ground state energy of the two-electron system (hydrogen-like molecule) and equation (12) is the equivalent for the threshold (hydrogen-like molecular ion) energy. If we keep $R \gg 1$ constant and move Z, we can find the critical line defined by $E_{0p}^{\mathrm{H}_2}(Z_c(R), R) = E_{0p}^{\mathrm{H}_2^+}(Z_c(R), R)$. This yields

$$Z_c^p(R) = -\frac{1}{R} + \sqrt{\frac{1}{R^2} + \frac{2}{R}}. \tag{13}$$

Another interesting issue is the asymptotic behaviour of the ground state energy near the critical line. We can define a critical exponent (α) for the energy as follows [13]:

$$I(Z, R) \sim (Z - Z_c)^{\alpha}, \qquad Z \to Z_c^+, \tag{14}$$

where $I(Z, R) = E_0(Z, R) - E_0^+(Z, R)$. With this purpose we expand the difference of energy $I_p(Z, R) = E_{0p}(Z, R) - E_{0p}^+(Z, R)$ around Z_c for a fixed value of the internuclear distance R. Then we find that for $R \gg 1$, the exponent is $\alpha = 1$.

Now we obtain some results for $R \to 0$. We know that the two-electron system energy over the critical line is equal to the threshold energy. The united atom limit (UAL) for the H_2^+ ground state energy is also well known [22]:

$$E_{\mathrm{UAL}}(Z_c(R), R) = -2Z_c^2 + \tfrac{8}{3}R^2 Z_c^4 - \tfrac{16}{3}R^3 Z_c^5 + O(R^4). \tag{15}$$

We can derive this expression for the energy over the critical line. Using the Hellmann–Feynman theorem, straightforward calculations lead to $\mathrm{d}Z_c(R)/\mathrm{d}R|_{R=0} = 0$. In addition, the well-known critical charge and critical exponent for the helium-like atom are [23, 24], $Z_c(R = 0) = 0.455\,514$ and $\alpha(R = 0) = 1$, respectively.

Using the results of section (2) and [15], we obtain an upper bound to the ground state energy of the Hamiltonian (1) as a function of the Hamiltonian parameters $E_0^{\mathrm{H}_2}(R, Z)$. The critical line ($Z_c(R)$) corresponding to the ionization threshold is defined by the condition $E_0^{\mathrm{H}_2}(Z_c(R), R) = E_0^{\mathrm{H}_2^+}(Z_c(R), R)$. The ground state stability diagram is shown in figure 1. This figure shows that the numerical results agree well with the previous discussion. The exponent α can be calculated using a finite size scaling (FSS) ansatz for quantum few-body systems [13, 25]. This approach has been successfully used for the determination of the critical behaviour of several atomic and molecular systems [11–13, 24, 26]. We used FSS to compute the critical exponent for a wide range of the internuclear distance. We obtained the value $\alpha = 1.00 \pm 0.01$ for $0.4 < R < 6.0$. This numerical result together with the previous discussion suggests that the critical exponent is $\alpha = 1$ for all values of R.

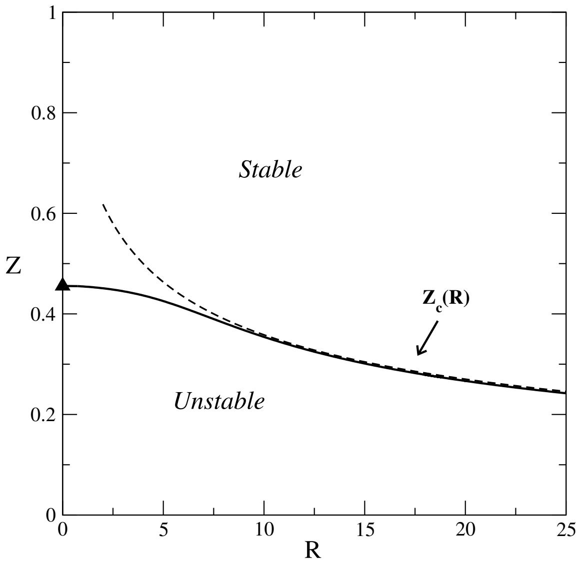

Figure 1. Ionization line for the homonuclear two-electron two-centre system. The full line shows numerical results. The dashed line shows the first-order perturbation expansion, valid for $R \gg 1$, and the triangle represents the critical value for the helium-like atom.

4. Ground state stability diagram for diatomic molecules

The complete Hamiltonian of the diatomic molecule in the Born–Oppenheimer approximation including the repulsion between the nuclear charges, in atomic units, is given by

$$H(R, Z_a, Z_b) = H_e(R, Z_a, Z_b) + \frac{Z_a Z_b}{R}, \tag{16}$$

where H_e is defined in equation (1) and the last term is responsible for the existence of a minimum in the energy as a function of the internuclear distance. In order to calculate the ground state energy and other observables of this system, we must repeat the procedure of section 3 taking into account that there is no restriction over q_n and s_n.

The ground state energy of the diatomic two-electron molecule is defined as

$$E_0(Z_a, Z_b; R_{\mathrm{eq}}) = \min_R (E_0(Z_a, Z_b; R)), \tag{17}$$

where $E_0(Z_a, Z_b; R)$ is the lowest eigenvalue of the Hamiltonian (16). It is clear that the ground state energy of the two-electron diatomic molecule is a function of the nuclear charges. As we move the value of these charges, the potential energy curves (PECs) suffer continuous deformations. The main goal of this section is to identify the PEC with stable or unstable configuration, determine and locate the different stability regimes. The stability diagram for the ground state in the $Z_a - Z_b$ plane is divided into four different regions. In the first one where the two-electron diatomic molecule is completely stable, as we know, is located the hydrogen molecule ($Z_a = Z_b = 1$). For lower values of the nuclear charges, the two Coulomb centre potential cannot bind two electrons. The line between these regions corresponds to the ionization line of the two-electron molecule. In the low-charge regime, the two-electron diatomic molecule is unstable, and the stable configuration corresponds to a two-centre one-electron system. The situation is different when we increase the nuclear charges. The repulsion between the nuclei increases, and we reach a situation where the Hamiltonian supports a normalized two-electron wavefunction, but equation (17) does not have solutions for finite values of R_{eq}, describing the dissociation of the diatomic molecule. In this situation, the two-electron diatomic molecule becomes unstable in a different way. Now the stable configuration corresponds to an atomic configuration. There exist two different dissociation regimes, the metastable and the completely unstable picture.

We can find the critical lines that divide these regions by numerical calculation of the PECs for different values of the nuclear charges.

(i) *Ionization line*

The system is stable against ionization when the two-electron diatomic molecule energy is lower than the one-electron two-centre system energy (threshold energy). Then, the ionization line is defined by

$$E_0^{\mathrm{H}_2}\left(Z_a, Z_b; R_{\mathrm{eq}}^{\mathrm{H}_2}\right) - E_0^{\mathrm{H}_2^+}\left(Z_a, Z_b; R_{\mathrm{eq}}^{\mathrm{H}_2^+}\right) = 0. \tag{18}$$

For charges lower than the critical charges, the ground state corresponds to a hydrogen-like molecular ion (H_2^+).

(ii) *Dissociation line*

Stable–metastable (SM) line

The system is completely stable against dissociation where the PECs have a global minimum for a finite internuclear distance. We define the SM line, that divides the stable molecular configuration from a metastable configuration, where the PECs have a local minimum for finite internuclear distance but the global minimum is located at $R = \infty$, as follows:

$$E_0^{\mathrm{H}_2}\left(Z_a, Z_b; R_{\mathrm{eq}}^{\mathrm{H}_2}\right) - \min\left[E_0^{\mathrm{He}}(\max[Z_a, Z_b]), E_0^{\mathrm{H}}(Z_a) + E_0^{\mathrm{H}}(Z_b)\right] = 0, \tag{19}$$

where $E_0^{\mathrm{He}}(Z)$ and $E_0^{\mathrm{H}}(Z)$ are the ground state energies of the helium-like atom and the hydrogen-like atom, respectively. It is interesting to note that this transition can occur in different ways. We have a symmetric dissociation in which each nuclear charge carries one electron and the result is two hydrogen-like atoms, and an asymmetric dissociation in which both electrons stay with one of the nuclear charges (the stronger) and the final situation is a helium-like atom plus a 'proton'. This kind of metastable situations could correspond with resonances when the Born–Oppenheimer approximation is removed.

Metastable–unstable (MU) line

Finally, the transition from a metastable to an unstable situation occurs when the local minimum is no longer present in the PEC. In the complete unstable situation, we just have one minimum at $R = \infty$.

As we discussed before, variational calculations become less accurate as we increase the internuclear distance. For this reason the numerical calculations in these regions were supported by calculations of the PECs using the DQMC method, to check the validity of the variational results.

The ground state stability diagram in the Z_a–Z_b-plane is shown in figure 2. Clearly, the stability diagram is symmetric around the line $Z_a = Z_b$. In the central part of the graphic, we can observe the stable zone (I). Two real molecules are located in this region, the hydrogen molecule (full circle) and the helium hydride molecular ion (HeH^+, full square). For small values of nuclear charges, we can recognize the ionization line (dotted-dashed line). This line starts and finishes in two triangles that correspond to the critical charge of the two-electron atom (for $Z_{a,b} = 0$, we have $Z_{b,a}^{\mathrm{ionization}} = 0.911\,028$ [23, 24]). Below this line, in

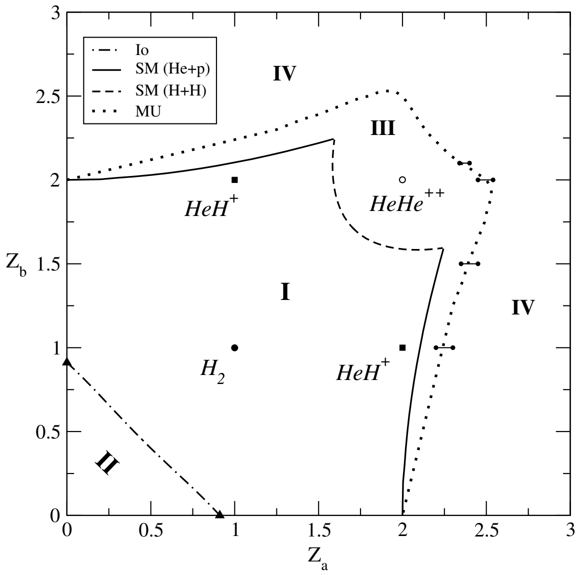

Figure 2. Ground state stability diagram of the diatomic two-electron molecule. The dashed and full lines show the dissociation to hydrogen-like atoms and to helium-like atom respectively (SM line). The dotted line represents the MU line. Points calculated by the DQMC with their corresponding error band are also showed (double points). The ionization line (Io) is represented by a dotted-dashed line. The endpoints (full triangles) of this line represent the critical charge for the helium-like atom.

the region (II), we have a one-electron two-centre system (hydrogen-like molecular ion) as a stable configuration. The critical conditions of such a system have been completely studied by Hogreve in [27], a work that was an important motivation for this section. For increasing values of the internuclear distance, we find the SM line. For symmetric molecules we have dissociation to hydrogen-like atoms (dashed line) and for asymmetric molecules dissociation to helium-like atom (continuous line). Finally, the outer line (dotted line) represents the MU line. Between these lines we have the region (III) where the system is metastable. The outer region corresponds to the unstable situation (IV). We can appreciate in (III) that the double cation helium–helium (He_2^{++}, empty circle) is the unique metastable diatomic two-electron molecule, in agreement with other works [4, 8]. The dissociation of extremely asymmetric systems can be solved analytically. It is straightforward to show that

$$\lim_{Z_{a,b}\to 0} Z_{b,a}^{\mathrm{Dissociation}} = 2 \tag{20}$$

for the SM and MU lines. Some points over the MU line calculated using the DQMC method are also shown in figure 2. They show a good agreement with the variational results.

5. Conclusions

We have shown a complete analysis of the ground state stability diagram for the two-centre two-electron diatomic molecules in the Born–Oppenheimer approximation.

We performed a detailed study of the ground state stability for a two-electron two-centre homonuclear system. We obtained the stability diagram and critical exponents using both numerical calculations and analytic approximations. Numerical data are in complete agreement with the analytical results.

The inclusion of the nuclear charge repulsion term gives us a more interesting scenario. Finally, we obtained the complete ground state stability diagram for diatomic two-electron molecules.

As might be expected, the new method for the evaluation of two-centre two-electron energy [15] gives us enough accuracy for calculations in a wide region of Hamiltonian parameters. In regions where we cannot ensure this accuracy, we complete our calculations with a totally different method (DQMC), obtaining great fidelity in our results.

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