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Exact non-Born-Oppenheimer wave function for the Hooke-Calogero model of the H_2 molecule

A useful exact molecular model for electron correlation studies

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Abstract. The Hooke-Calogero model of the H_2 molecule, a four body system consisting of two protons and two electrons with harmonic electron-nuclear, Coulombic electron-electron and inverse quadratic nuclear-nuclear interactions, has been analyzed in–depth. A fully analytical closed–form non-Born-Oppenheimer solution has been found and based on it the properties of both electron–pair and nuclear–pair densities have been studied. Nuclei have been found to be strongly correlated in a way that resembles a sort of Wigner crystallization, for moderate electron–nucleus confinement strengths. Additionally, we have explicitly evaluated the Coulomb holes for the electrons. Analysis of these holes reveals that the similarity between the electron correlation effects of the model as compared to the real Coulombic systems is remarkable.

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1 Introduction

The Schrödinger equation for most N-body physical systems of interest is either non-separable or leads to one-particle equations which cannot be solved analytically. This difficulty is quite often circumvented through the introduction of models for which analytic solutions are available. Clearly, analytic solutions are quite useful, not only for the purpose of finding closed-form expressions for physical variables — such as the energy and its various components, the one-particle density, etc. which can be then related to and contrasted with experimental measurements — but also because they provide exact values against which results obtained from approximate theoretical methods can be calibrated.

The renewed interest in solvable and quasi-solvable models in several areas of physics is a clear indication as to their actual or potential usefulness. In this vein, Johnson [1] has reviewed some solvable models applicable to quantum dots. More recently, Bose and Gupta have given a comprehensive treatment of different types of solvable potentials [2]. Similarly, based on group theoretical considerations, Tanaka [3] has discussed a systematic procedure for the generation of solvable and quasi-solvable models. In the present work, we adopt the Hooke-Calogero model to carry out an exact analytic treatment of H_2 molecule. In this model, a harmonic potential replaces the electron-nuclear interaction (Hookean model) and an inverse square potential substitutes the nuclear-nuclear one (Calogero model). As we shall show below, although this model contains simplifications that make the problem mathematically tractable, it includes, nevertheless, some of the essential aspects of the real Coulombic H_2 molecule.

The introduction of harmonic confining potentials to replace, at various levels of approximation, the actual Coulomb interactions between charged particles, such as electrons and nuclei, or to mimic the effects of confining fields, etc., has been a long-standing practice. Thus, for example, when all interactions in an atom are replaced by harmonic potentials, we have what is generally called the Moshinsky model [4]. In the Hookean atom (or harmonium) only the electron-nuclear potentials are replaced by harmonic ones (the electron-electron potentials remain Coulombic). The two-electron Hookean atom is quite an interesting problem as there exists a set of discrete values of the harmonic coupling parameter for which analytic solutions to the relative electron motion equation can be found [5–12]. Because these solutions do not exhaust the realm of all possible ones [13], the problem is only quasi-solvable. The results for the Hookean two-electron atom, however, cannot be readily generalized. On the one hand, the generalization to larger number electrons has been

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proven to be difficult. For instance, for three electrons with full Coulomb interaction confined in a harmonic well, only approximate solutions may be obtained [14]. On the other hand there are a number of processes, like molecular dissociation, that cannot be addressed by the present harmonic confining potential model.

Another model leading to solvable problems is based on the inverse-square potential. This type of potential already appears in the Fues-Kratzer model (for a recent application, see Ref. [15]). However, the inverse square potential is customarily associated with the name of Calogero [16–19], or, when extensions are made to encompass periodic boundary conditions, with that of Calogero-Sutherland [20] in view of the exact treatments presented by these authors of the N-particle problem in one-dimension. As a recent application of this model, we may mention the determination of the particle-number fluctuation and its relation to correlation strength [21]. For an exactly solvable variant of the Calogero-Sutherland model, see reference [22]. Inverse square potentials in three-dimensions are particularly important as they approach or are close to real potentials in asymptotic limits. For this reason, they have been used in the context of the Faddeev treatment of the three-body system, for which exact solutions have been obtained [23]. In addition, they have been used to approximate the real Coulomb potential through the first term of the identity $a/r = b/r^2 + (ar - b)/r^2$ for the case two-interacting electrons in a three-dimensional parabolic quantum dot [24]. Analytic results for two-dimensional N-particle systems interacting through $1/r^2$ potentials in the presence of a magnetic field have been obtained by Johnson and Quiroga [25]. A model of three electrons moving in a plane with Calogero interactions shows excellent agreement with calculations using the exact interaction in a parabolic quantum dot [26].

We present here an exact non–relativistic analytic solution to the Hooke-Calogero model of the diatomic molecules H_2, which we take to be a four particle system of the type $M^+M^+m^-m^-$ (where M^+ denotes a proton and m^- an electron) with harmonic interaction between the M^+m^- pairs, a Coulombic interactions between the electrons and an inverse square interaction between the protons. Quite recently [27], we have examined a Hookean model for H_2, where, again, the M^+m^- interactions were assumed to be harmonic, but where the remaining ones were taken to be of the exact Coulomb type. Although in that case there is a decoupling of the Schrödinger equation into separate equations for the relative motion of electrons and nuclei, exact analytic solutions cannot be obtained simultaneously for both equations due to the existence of an indirect link between the harmonic coupling constants appearing in both equations. Thus, a particular value of the coupling constant that allows us to obtain an analytic solution of the relative motion of electrons produces a coupling constant for the relative motion of nuclei for which there is no analytic solution. This difficulty is lifted in the present case by resorting to the inverse square interaction for the protons (i.e., by introducing a Calogero-type potential). As a consequence, we are able to present, for the *first time*, a fully non–relativistic analytic non-Born-Oppenheimer solution for a model of the H_2 molecule. We can think of the present Hooke-Calogero model as sort of a “poor man’s molecule”which can be used, in the same way as the Hooke model for the helium atom has been used [28,29], for the purposes of learning more about electron correlation effects.

In Section 2, we show how the Hamiltonian is decoupled. In Section 3, we present the — largely textbook — solutions to the decoupled equations. For completeness, however, we show that the usual solution to the three-dimensional harmonic oscillator is also valid for the case on non-integer angular momentum (centrifugal) quantum numbers. In Section 4, we analyze the electron and nuclear intracule densities. In Section 5, we compare the present results with those of the Hookean H_2 molecule. Finally, in Section 6 we summarize the conclusions.

2 Separation of the Hamiltonian

For the Hooke-Calogero model of H_2, described above, the non–relativistic Hamiltonian operator (in units of $\hbar = m = e = 1$) is:

$$\begin{aligned}\widehat{H} = &-\frac{1}{2M}\nabla^2_{\mathbf{R}_A} - \frac{1}{2M}\nabla^2_{\mathbf{R}_B} - \frac{1}{2}\nabla^2_{\mathbf{r}_1} - \frac{1}{2}\nabla^2_{\mathbf{r}_2}\\ &+ \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} + \frac{1}{|\mathbf{R}_A - \mathbf{R}_B|^2}\\ &+ \frac{\omega^2}{2}(\mathbf{r}_1 - \mathbf{R}_A)^2 + \frac{\omega^2}{2}(\mathbf{r}_1 - \mathbf{R}_B)^2\\ &+ \frac{\omega^2}{2}(\mathbf{r}_2 - \mathbf{R}_A)^2 + \frac{\omega^2}{2}(\mathbf{r}_2 - \mathbf{R}_B)^2 \end{aligned} \tag{1}$$

where from an arbitrary reference system, $\mathbf{R}_A$ and $\mathbf{R}_B$ are the position vectors for the protons (M^+) A and B, and $\mathbf{r}_1$ and $\mathbf{r}_2$, those of electrons (m^-) 1 and 2, respectively.

The Schrödinger equation for this system

$$\widehat{H}\Psi(\mathbf{R}_A, \mathbf{R}_B, \mathbf{r}_1, \mathbf{r}_2) = E\Psi(\mathbf{R}_A, \mathbf{R}_B, \mathbf{r}_1, \mathbf{r}_2) \tag{2}$$

is separable in terms of the relative coordinates of the nuclei $\mathbf{R}$, the relative coordinates of the electrons $\mathbf{r}$, a collective translation coordinate $\mathbf{P}$ and a pseudo-particle coordinate $\mathbf{Q}$ which are related to the initial coordinates by:

$$\mathbf{R} = \mathbf{R}_A - \mathbf{R}_B \tag{3}$$

$$\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2 \tag{4}$$

$$\begin{bmatrix}\mathbf{P}\\ \mathbf{Q}\end{bmatrix} = R(\theta)\begin{bmatrix}(\mathbf{r}_1 + \mathbf{r}_2)/2\\ \sqrt{M}(\mathbf{R}_A + \mathbf{R}_B)/2\end{bmatrix} \tag{5}$$

being $R(\theta)$ a unitary rotation of angle $\theta = \tan^{-1}\sqrt{M}$. Details of the derivation of the decoupling coordinates $\mathbf{P}$ and $\mathbf{Q}$ are given in [27] (see also Ref. [30]). In terms of these coordinates, the Hamiltonian decouples into:

$$\widehat{H} = \widehat{H}_{\mathbf{R}} + \widehat{H}_{\mathbf{r}} + \widehat{H}_{\mathbf{P}} + \widehat{H}_{\mathbf{Q}}. \tag{6}$$

Rewriting the wave function as

$$\Psi(\mathbf{R}_A, \mathbf{R}_B, \mathbf{r}_1, \mathbf{r}_2) = \Psi_{\mathbf{R}}(\mathbf{R})\Psi_{\mathbf{r}}(\mathbf{r})\Psi_{\mathbf{P}}(\mathbf{P})\Psi_{\mathbf{Q}}(\mathbf{Q}) \qquad (7)$$

we obtain through separation of variables the following set of equations:

$$\Big(-\nabla^2_{\mathbf{r}} + \frac{1}{r} + \frac{\omega^2}{2}r^2\Big)\Psi_{\mathbf{r}}(\mathbf{r}) = E_{\mathbf{r}}\Psi_{\mathbf{r}}(\mathbf{r}) \qquad (8)$$

$$\Big(-\frac{1}{M}\nabla^2_{\mathbf{R}} + \frac{1}{R^2} + \frac{\omega^2}{2}R^2\Big)\Psi_{\mathbf{R}}(\mathbf{R}) = E_{\mathbf{R}}\Psi_{\mathbf{R}}(\mathbf{R}) \qquad (9)$$

$$-\frac{1}{2}\nabla^2_{\mathbf{P}}\Psi_{\mathbf{P}}(\mathbf{P}) = E_{\mathbf{P}}\Psi_{\mathbf{P}}(\mathbf{P}) \qquad (10)$$

$$\Big(-\frac{1}{2}\nabla^2_{\mathbf{Q}} + \frac{4(M+1)\omega^2}{M}Q^2\Big)\Psi_{\mathbf{Q}}(\mathbf{Q}) = E_{\mathbf{Q}}\Psi_{\mathbf{Q}}(\mathbf{Q}) \qquad (11)$$

where the total energy, E, of equation (2) is,

$$E = E_{\mathbf{r}} + E_{\mathbf{R}} + \frac{E_{\mathbf{Q}} + E_{\mathbf{P}}}{2}. \qquad (12)$$

The solutions of the integro-differential equation corresponding to the relative motion of the electrons, equation (8), have been found earlier for the Hookean He atom [6,11,13] and for the Hookean H_2 molecule [27] and, those corresponding to the collective coordinates, equations (10, 11), have been discussed recently [27] within the context of the Hookean H_2. Indeed equations (8–11) are very similar to those of the Hookean H_2 (see Eqs. (5, 6, 12–14) of Ref. [27]) but they bear one very important difference which stems from the power of relative coordinate of the nuclei, R. For the Hookean H_2, the interaction between the two nuclei is Coulombic yielding R^{-1}. Consequently the Hamiltonians governing the relative motions of both electrons and nuclei became formally equivalent, with the sole difference of their masses and the effective confinement strength parameter, $W_T^2 = \omega^2/2$ for the electrons and $W_T^2 = M \times \omega^2/2$ for the nuclei. However, this has a big effect, for Taut [11] demonstrated that analytical closed–form solutions for such a Hamiltonian exist only for a discrete set, $\{\mathsf{A}\}$, of values of the confinement strength parameter W_T. Therefore, for the Hookean H_2 molecule we obtain two separate sets of confinement parameters for which the relative motion Hamiltonian has analytical closed–form solutions, namely:

$$\{\omega^R\} = \{\omega \mid \omega = \sqrt{2/M}\, W_T \mid W_T \in \{\mathsf{A}\}\} \qquad (13)$$

$$\{\omega^r\} = \{\omega \mid \omega = \sqrt{2}\, W_T \mid W_T \in \{\mathsf{A}\}\}. \qquad (14)$$

We have found [27] that these two sets are disjoint:

$$\{\omega^R\} \cap \{\omega^r\} = \emptyset. \qquad (15)$$

Consequently, for the Hokeean H_2 molecule, given a confinement strength parameter ω, *there do not exist analytical closed–form solutions for both nuclei and electrons simultaneously.* If we chose analytical closed–form solutions for either nuclei or electrons, then approximate solutions for the other set of particles must be sought.

This constraint may be lifted by replacing the internuclear interaction potential. Thus, if instead of the Coulombic potential, the inverse–square potential is set for the interaction between the nuclei, as it has already been done in equation (1), then the resulting equations (8–11) bear full analytical closed–form solutions.

In the following section we elaborate the solution of the Hooke-Calogero Hamiltonian for the relative motion of the nuclei, equation (9).

3 Relative motion of nuclei

Let us rewrite equation (9) as:

$$\left(-\frac{1}{2}\nabla^2_{\mathbf{R}} + \frac{M}{2R^2} + \frac{W_R^2}{2}R^2\right)\Psi_{\mathbf{R}}(\mathbf{R}) = E'_{\mathbf{R}}\Psi_{\mathbf{R}}(\mathbf{R}) \qquad (16)$$

where $W_R \equiv \sqrt{M/2}\times\omega$ and $E'_{\mathbf{R}} = M\,E_{\mathbf{R}}/2$. Assume that $\omega \in \{\omega^r\}$. In this manner, we guarantee that the radial equation of the relative motion of electrons has an analytic solution and now we will seek an analytical solution for the relative motion of the nuclei.

Equation (16) can be separated into a radial part and an angular part by assuming that

$$\Psi_{\mathbf{R}}(\mathbf{R}) = \psi_R(R) Y_{l_R,m_R}(\theta_R, \varphi_R). \qquad (17)$$

The equation for the radial function $\mu_R(R) \equiv R\psi_R(R)$ can be put into the form

$$\left(-\frac{1}{2}\frac{d^2}{dR^2} + \frac{l_R(l_R+1)}{2R^2} + \frac{M}{2R^2} + \frac{W_R^2}{2}R^2\right)\mu_R(R) = E'_R\mu_R(R). \qquad (18)$$

Since the second and third terms in the above equation have the same R^{-2} dependence, we can bring them together by introducing the non-integer pseudo quantum number (for a similar procedure, see the Appendix of Ref. [24])

$$\widetilde{l}_R = l_R + \alpha \qquad (19)$$

satisfying the equation

$$\widetilde{l}_R(\widetilde{l}_R + 1) = l_R(l_R + 1) + M. \qquad (20)$$

The value of α that fulfills this condition is

$$\alpha = -l_R + \frac{-1 \pm \sqrt{(2l_R+1)^2 + 4M}}{2} \qquad (21)$$

(let us comment here that the introduction of modified quantum numbers in equations describing atomic levels is indeed very old and forms the basis for what is called quantum–defect theory [31–35]). The resulting equation

$$\left(-\frac{1}{2}\frac{d^2}{dR^2} + \frac{\widetilde{l}_R(\widetilde{l}_R+1)}{2R^2} + \frac{W_R^2}{2}R^2\right)\mu_R(R) = E'_R\mu_R(R) \qquad (22)$$

is that of a three-dimensional harmonic oscillator. However, equation (22) differs from the usual one in that $\widetilde{l}_R$ is not a quantum number, i.e., it is not an integer (in fact, it is a function of the quantum number l_R). Nevertheless, as we show below, the usual solution to the three-dimensional harmonic oscillator also applies to the case of non-integer $\widetilde{l}_R$. To this effect, we consider the trial solution (where for simplicity we drop the subindex R)

$$\mu_l(R)=v_l(R)R^{\widetilde{l}+1}\exp\left(-\frac{W_R}{2}R^2\right). \tag{23}$$

This trial function yields the following differential equation for $v_l(R)$ [36]:

$$-\frac{1}{2}\frac{d^2v_l(R)}{dR^2}-\left[\frac{(\widetilde{l}+1)}{R}-W_RR\right]\frac{dv_l(R)}{dR}+\left[-E'_R+W_R\left(\widetilde{l}+\frac{3}{2}\right)\right]v_l(R)=0 \tag{24}$$

from which by letting $z=W_RR^2$ and $w_l(z)\equiv v_l(R)$ we obtain Kummer's equation (i.e., Eq. (13.1.1) of Abramowitz and Stegun [37])

$$z\frac{d^2w_l(z)}{dz^2}+(b-z)\frac{dw_l(z)}{dz}-aw_l(z)=0 \tag{25}$$

where $b=(\widetilde{l}+3/2)$ and $a=(\widetilde{l}+3/2)/2-E'_R/(2W_R)$. The solution is clearly $w_l(z)=M(a,b,z)$. Now, since according to equation (13.1.4) of reference [37], the confluent hypergeometric function can be expressed as

$$M(a,b,z)=\frac{\Gamma(b)}{\Gamma(a)}e^zz^{a-b}[1+O(|z|^{-1})];\ \mathcal{R}\mathrm{eal}(z)>0 \tag{26}$$

when $z\to\infty$, integrability of $M(a,b,z)$ requires that $\Gamma(a)=\infty$. As the poles of $\Gamma(a)$ occur at the values $-a=0,1,2,\ldots$, it follows that

$$\frac{1}{2}\left(\widetilde{l}+\frac{3}{2}\right)-\frac{E'_R}{2W_R}=-v;\ v=0,1,2,\ldots \tag{27}$$

The non-integer condition of $\widetilde{l}$ is then transferred to the energy expression:

$$E_R=\sqrt{\frac{2}{M}}\left[\left(\widetilde{l}_R+\frac{3}{2}\right)+2v_R\right]\omega \tag{28}$$

which is obtained after the replacements $W_R=\sqrt{M/2}\omega$ and $E'_R=M\,E_R/2$ are made. In conclusion, the explicit general form of the radial function appearing in equation (17) is:

$$\psi_{v_R,l_R}(R)=N_{v_R,l_R}M(-v_R,\widetilde{l}_R+3/2,W_RR^2)R^{\widetilde{l}_R}\times\exp\left(-\sqrt{\frac{M}{8}}\omega R^2\right) \tag{29}$$

(where, again, we have written explicitly the subindex R to denote that these quantities pertain to the relative coordinate R and to distinguish them from the quantum numbers n_r and l_r relative to electronic motion).

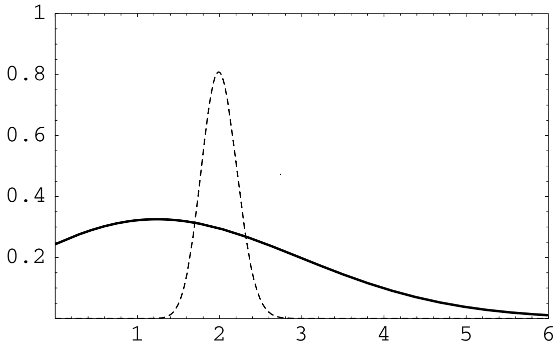

Fig. 1. Comparison between the wavefunctions of the electron relative motion ($\psi_{1,0}(r)$ and of the nuclear relative motion $\psi_{0,0}(R)$, Eq. (30)) for the Hooke-Calogero H_2 molecule with $\omega=\sqrt{2}/4$ in equation (1).

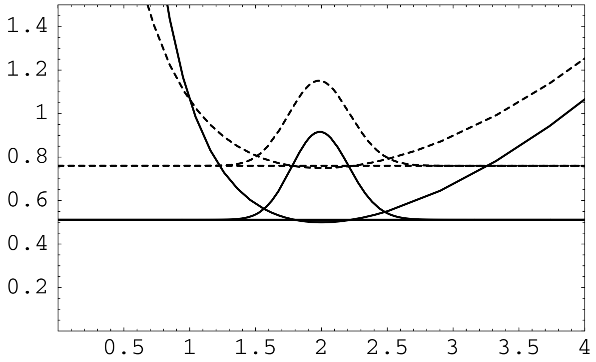

Fig. 2. Nuclear potential and the nuclear wavefunction $\psi_{0,0}(R)$ according to equation (30). The horizontal line indicates the value of the E_R energy for the nuclear relative motion. Solid lines correspond to the present Hooke-Calogero H_2 molecule. Dashed lines represent the nuclear potential, the nuclear wavefunction and the nuclear relative motion energy for the Hookean H_2 molecule as calculated in reference [27].

Let us consider the particular case when $n_r=1$ and $l_r=0$ for which at $\omega=\sqrt{2}/4\in\{\omega^r\}$ the Hamiltonian for relative motion of the electrons has a closed–shell analytical solution [27]. Then, taking for the proton mass the value of 1836 electron masses, it follows from equations (19) and (21), that when the quantum number $l_R=0$ we obtain $\widetilde{l}_R\simeq 42.3515$. Hence, when in addition we set $v_R=0$, in view of the fact that $M(0,b,R)=1$, $\forall\,(b,R)$, the wavefunction becomes:

$$\psi_{0,0}(R)=N_{0,0}R^{42.3515}\exp\left(-5.356R^2\right). \tag{30}$$

This is a highly peaked function of the relative nuclear motion coordinate as shown in Figure 1. Using this wavefunction, we can calculate the value of R for which the probability to find the nuclei is maximum, and we obtain a value of $R_{max}=2.012$ Bohr. Recall that the corresponding maximum probability internuclear distance for Hookean H_2 is attained [27] at $R=2.009$ Bohr. This indicates that in spite of the different interaction potentials the resulting wavefunctions are similar. This is illustrated

Table 1. Energy for the electronic and nuclear relative motions and their kinetic, repulsion and confinement components. For completeness, the energies for the nuclear relative motion in the Hookean H_2 case are also reported as calculated in reference [27].

Calc. type	Total energy	Energy components		
		kinetic	repulsion	confinement
$E_{\mathbf{r}}$		Electron relative motion		
	1.250000	0.289418	0.447443	0.513139
$E_{\mathbf{R}}$		Nuclear relative motion		
Hooke-Calogero	0.511703	0.005868	0.249983	0.255851
Hookean H_2 [27]	0.760132	0.005079	0.499982	0.255070
		Quasiparticle harmonic motion		
$E_{\mathbf{Q}}$	0.750204			

in Figure 2 which shows the wavefunctions of the relative nuclear motion for both the Hooke and the Hooke-Calogero models of H_2.

4 Total wavefunction and total energy

Coordinate $\mathbf{P}$ describes the collective motion of a free particle. The internal energy is measured taking as a reference this free-particle energy, namely, assuming that $E_{\mathbf{P}} = 0$. Incidentally, this choice, in view of equation (10) reduces $\Psi_{\mathbf{P}}$ to a constant will be subsumed into the normalization constant. Thus, considering separately the radial and angular coordinates, like in equation (17), of the remaining wavefunctions of the product equation (7) we may rewrite the total wavefunction as:

$$\Psi(\mathbf{R}_A, \mathbf{R}_B, \mathbf{r}_1, \mathbf{r}_2) = \psi_{n_r,l_r}(r)\psi_{\upsilon_R,l_R}(R)\psi_{\upsilon_Q,l_Q}(Q) \times Y_{l_r,m_r}(\theta_r, \varphi_r)Y_{l_R,m_R}(\theta_R, \varphi_R)Y_{l_Q,m_Q}(\theta_Q, \varphi_Q). \quad (31)$$

It follows, therefore, that the total wavefunction depends on the coordinates of the relative electron and nuclear motions, r and R, respectively, on the coordinate Q of the quasi-particle motion and on six angles. In principle, it is possible to transform these angles into the usual three Euler angles describing the rotation of the system as a whole plus three angles that describe the internal rotations. This, of course, would allow us to define total quantum numbers for the rotation. As evinced from the difficulties one encounters in obtaining these quantum numbers for the three-particle problem, one would expect that this reduction is not trivial in the present case. For this reason, we discuss the total solution disregarding all angular motion. In other words, we take the lowest values of the angular momentum quantum numbers in all these cases: $l_r = 0$, $m_r = 0$, $l_R = 0$, $m_R = 0$, $l_Q = 0$ and $m_Q = 0$. Moreover, we also take the lowest allowed values of the quantum numbers $n_r = 1$, $\upsilon_R = 0$ and $\upsilon_Q = 0$. The total wavefunction for this case becomes:

$$\Psi(\mathbf{R}_A, \mathbf{R}_B, \mathbf{r}_1, \mathbf{r}_2) = \mathcal{N}\left(1 + \frac{r}{2}\right) R^{(-1+\sqrt{1+4M})/2} \times \exp\left(-\frac{r^2}{8} - \sqrt{\frac{M}{8}}R^2 - \sqrt{\frac{M+1}{4M}}Q^2\right). \quad (32)$$

The total energy, see equation (12), is

$$E = E_{\mathbf{r}} + E_{\mathbf{R}} + \frac{E_{\mathbf{Q}}}{2} \quad (33)$$

as we have set $E_{\mathbf{P}} = 0$. For $n_r = 1$ and $l_r = 0$, the energy of the relative electronic motion becomes

$$E_{\mathbf{r}} = \frac{5}{4}. \quad (34)$$

For the relative nuclear motion the energy for $\upsilon_R = \tilde{l}_R = 0$ and $\omega = \sqrt{2}/4$ is, in accordance with equations (21, 28):

$$E_{\mathbf{R}} = \frac{1}{2}\sqrt{\frac{4M+1}{4M}} + \frac{1}{\sqrt{4M}}. \quad (35)$$

For $M = 1836$ electron masses, $E_{\mathbf{R}} = 0.511703$ a.u. The values of the kinetic, repulsion and confinement components of $E_{\mathbf{r}}$ and $E_{\mathbf{R}}$ are given in Table 1. For completeness, the values of the relative nuclear motion components for the case of the Hookean H_2 molecules are also included. Of course, for the Hooke-Calogero and the Hookean model of H_2, both the relative electronic motion and the quasiparticle motion (harmonic oscillator motion) are equal and they only differ in the nuclear motion energy.

Finally, the energy for the three-dimensional harmonic oscillator on the collective coordinate $\mathbf{Q}$, for $\upsilon_Q = l_Q = 0$ and $\omega = \sqrt{2}/4$ is:

$$E_{\mathbf{Q}} = \frac{3}{2}\sqrt{\frac{M+1}{M}}. \quad (36)$$

This completes all the terms of equation (33) and yields a total energy of,

$$E = \frac{10}{4} \quad (37)$$

for the infinite nuclear mass, $M \to \infty$ approximation. Recall that for the Hookean H_2 the corresponding total energy [27] is $E = 11/4$ and for the Hookean He atom [6], $E = 8/4$. Observe that the total energy of the Hooke-Calogero H_2 model is smaller than that of the Hooke model, because it bears less internuclear repulsion. Naturally, Hookean He is the most stable because it has no internuclear repulsion.

Table 2. Moments of the electronic and nuclear intracule densities.

	Electronic ($x = r$)		Nuclear ($x = R$)	
	Hooke-Calogero	Coulombic [40]	Hooke-Calogero	Hookean [27]
x_{max}	2.494	2.356	2.012	2.009
μ^2_{max}	0.393	0.363	2.614	2.434
$\langle x^{-2}\rangle$	0.276	0.355	0.250	0.252
$\langle x^{-1}\rangle$	0.447	0.477	0.499	0.500
$\langle x^{0}\rangle$	1.000	1.000	1.000	1.000
$\langle x^{1}\rangle$	2.685	2.664	2.018	2.014
$\langle x^{2}\rangle$	8.210	8.398	4.094	4.081
$\sigma = \sqrt{\langle x^2\rangle - \langle x\rangle^2}$	1.001	1.141	0.153	0.164

5 Electronic and nuclear intracule densities

In view of the decomposition of the wavefunction given by equation (7) the only wavefunction that depends explicitly on the relative electronic coordinate is $\Psi_r(\mathbf{r}) = \psi_r(r)/\sqrt{4\pi}$. For this reason, the electronic intracule density is straightforwardly evaluated as:

$$I_e(\mathbf{r}) = \langle \Psi \mid \delta(\mathbf{r} - \mathbf{r}_1 + \mathbf{r}_2) \mid \Psi \rangle = \frac{1}{4\pi} |\psi_r(\mathbf{r})|^2. \qquad (38)$$

The spherically averaged electronic intracule density is:

$$h_e(r) = \frac{1}{4\pi} \int d\Omega_r I_e(\mathbf{r}) \qquad (39)$$

and consequently, the electron–pair probability distribution is given by:

$$P_e(r) = 4\pi r^2 h_e(r) = r^2 |\psi_r(r)|^2 = |\mu_r(r)|^2. \qquad (40)$$

Similarly, for the relative nuclear motion we have in the present case

$$I_n(\mathbf{R}) = \langle \Psi \mid \delta\left(\mathbf{R} - \frac{\mathbf{R}_1 + \mathbf{R}_2}{2}\right) \mid \Psi \rangle = \frac{1}{4\pi} |\psi_R(R)|^2 \qquad (41)$$

and, since the spherically averaged nuclear intracule density is defined as

$$h_n(R) = \frac{1}{4\pi} \int d\Omega_R I_n(\mathbf{R}) \qquad (42)$$

the nucleus–pair probability distribution can be cast as:

$$P_n(R) = 4\pi R^2 h_n(R) = R^2 |\psi_R(R)|^2 = |\mu_R(R)|^2. \qquad (43)$$

In Table 2, we compare the momenta of both the electronic and nuclear intracule densities for the Hooke, Hooke-Calogero and Coulombic H_2 and, in Figure 3, we present graphs of the electron–pair and nucleus–pair probability distributions.

6 Comparison with the Hookean model for H_2

The Hookean model for H_2, in contrast with the present Hooke-Calogero model, adopts the true $1/R$ interaction between nuclei. However, as seen elsewhere [27], this choice of potential prevents us from truly decoupling the electronic and nuclear motions (which remain entangled through the connection of their respective harmonic coupling constants). The present choice of the $1/R^2$ potential allows us, on the other hand, to circumvent this problem. As a consequence, in this context, we are able to generate both the exact analytic wavefunction given by equation (32) and its associated energy, equation (33).

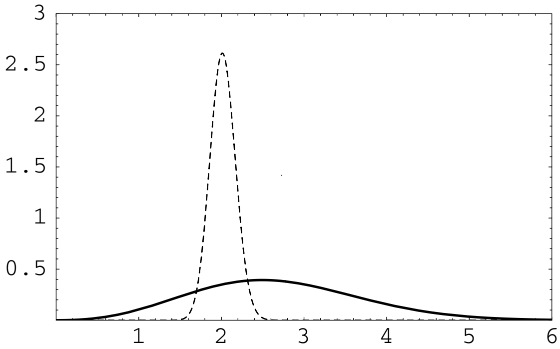

Fig. 3. Electron–pair (solid line) and nucleus–pair (dashed line) probability distribution functions for the Hooke-Calogero H_2 molecule with $\omega = \sqrt{2}/4$ in equation (1).

It is of interest, for this reason, to compare the present exact analytic results with approximate analytic wavefunctions obtained for the Hooke model of H_2. In this vein, in Table 1 we have included values of the relative nuclear motion components for the Hooke model of H_2. Also, in Table 2, we have included the momenta for the pair probability distributions of the latter model. In Figure 2 the nuclear potentials and their corresponding wavefunctions for both of these models are plotted. Finally, in Figure 4, we compare the Hooke-Calogero and Hooke nucleus–pair probability distributions.

It is seen in Table 1 that the effect of the inverse square potential for the nuclear motion does not affect significantly the kinetic and confinement energy components of the Hooke-Calogero model with respect to those of the Hookean model for H_2. In fact, the main difference arises in the repulsion energy which is twice as large for the Coulomb potential (0.4999982 Hartrees vs. 0.249983 Hartrees). However, in spite of this difference, as it is seen in Table 2, both models yield practically the same

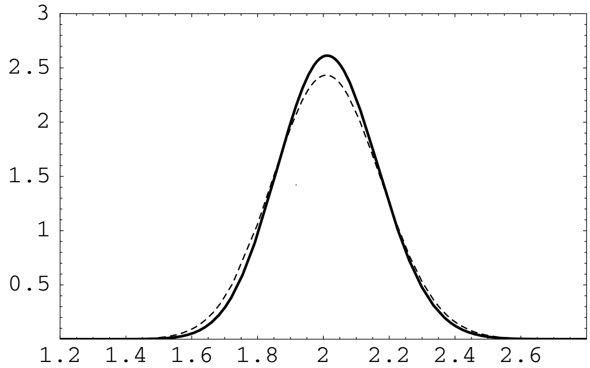

Fig. 4. Nucleus–pair probability distribution functions for the Hooke-Calogero H_2 molecule (solid line) and for the Hookean H_2 molecule (dashed line), with $\omega = \sqrt{2}/4$ in equation (1).

equilibrium distance (2.012 Bohr for the Hooke-Calogero model vs. 2.009 Bohrs for the Hookean one).

One sees in Figure 2 that the shape of the Hooke-Calogero potential is steeper at short values of the internuclear coordinate R. At large distances, both potentials show a similar behavior. As a consequence, the nuclear wavefunctions are quite similar although the Hooke-Calogero wavefunction appears to be slightly less disperse. This behavior is clearly reflected in the smaller standard deviation value of $\sigma = 0.153$ for the nuclear intracule density of the Hooke-Calogero model against $\sigma = 0.164$ for the Hookean one. It is important to note, in addition, that both these models lead to an extremely high localization of the nuclei. This is an example of the phenomenon of crystallization predicted by Wigner [38] in regimes dominated by very high correlation. In contrast, the standard deviation for the electronic intracule density is $\sigma = 1.001$. This value denotes a substantial delocalization of the electrons, even though the electrons are correlated through the function $(1 + r/2)$ (where r is the interelectronic coordinate).

In Figure 4 it is seen that the nucleus–pair probability distributions for both these models are almost coincident. This result, which is somewhat striking, has important practical consequences as it shows that the very complicated function [27] describing the nucleus–pair probability in the Hookean model of H_2 can be closely approximated by the much simpler analytical closed–form, equation (43), of the Hooke-Calogero model.

7 The Coulomb hole

The electron correlation [39] in general and the Coulomb hole in particular is one of the so–called *holy grails* of the electronic structure theory [40]. Having obtained an exact analytical solution for the Hooke-Calogero model of the H_2 molecule, one might think of using it to develop better strategies to deal with the electron correlation effects. However, this is pending on how similar or different are the *real* Coulombic Coulomb hole and the modeled Hooke-Calogero Coulomb hole.

Recall that the Coulomb is defined [41] as the difference between the *exact* and *Hartree–Fock* electron–pair probability distributions, namely, for the electrons:

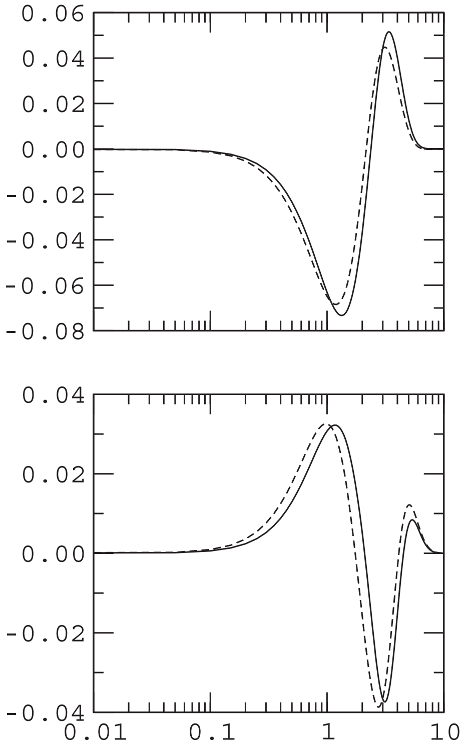

Fig. 5. Upper panel: Coulomb holes for the Hooke-Calogero model (dashed line) and the Coulombic (solid line) for the H_2 molecule at the internuclear distance $R = 2.012$ Bohr, as a function of the interelectronic distance. Lower panel: exact (solid line) and Hartree–Fock (dashed line) Coulombic minus Hooke-Calogero electron–pair probability distributions for the H_2 molecule at the internuclear distance $R = 2.012$ Bohr, as a function of the interelectronic distance.

$$\Delta P_e(r) = P_e^{ex}(r) - P_e^{HF}(r) \tag{44}$$

where P_e^{ex} is given by equation (40). The Hartree–Fock electron–pair probability distributions, $P_e^{HF}(r)$, for the Hooke-Calogero Hamiltonian of equation (1), has been calculated expanding the Hartree–Fock singlet ground state wavefunction in an orthonormal basis of Cartesian Gaussian. The resulting self–consistent problem has been solved iteratively. The calculated electron correlation energy of –33.841495 mHartree for the Hooke-Calogero model compares well with that of the Coulombic real H_2 system [40], –37.643987 mHartree. Notice that for He, the Hookean and Coulombic electron correlation energies are –38.438873 mHartree and –42.044000 mHartree, respectively [42]. The difference between the Hookean and Coulombic systems is, in both cases, ∼4 mHartree.

The upper panel in Figure 5 shows the Coulomb hole for the Hooke-Calogero model of the H_2 molecule calculated at a internuclear distance of 2.012 Bohr and the corresponding Coulombic Coulomb hole at the same internuclear distance. The similarity between both Coulomb holes is remarkable and supports the assertion of Kestner and Sinanoglu [5] that correlation effects are rather insensitive to the nature of the external confining field of the electrons. This point has also been recently made by O'Neil and Gill [42] in their analysis of the electron correlation for the Hookean He atom. However, as shown in the lower panel of Figure 5, this does not mean that the Coulombic and Hooke-Calogero electron–pair distributions are similar, but rather it turns out that electron correlation effects operate similarly in both Coulombic and Hooke-Calogero H_2 systems. Consequently, the Hooke-Calogero H_2 molecule might represent a convenient "poor man's"molecular system for modeling electron correlations effects occurring in real Coulombic systems. The latter point is further supported by the nice agreement between the electronic properties of both systems, as shown in Table 2.

8 Conclusions

An important and as yet unsolved problem in molecular quantum theory is the proper treatment of molecules in a non-Born-Oppenheimer framework. We present in this work an exact analytic solution based, precisely, on a non-Born-Oppenheimer treatment of a model of the hydrogen diatomic molecule. This model, called the Hooke-Calogero model introduces a harmonic interaction between electrons and protons and an inverse quadratic interaction between protons. This exact analytic solution is displayed in equation (32).

An important aspect of this solution is that it yields a highly peaked nuclear intracule distribution. Thus, in a natural way, the present non-Born-Oppenheimer treatment predicts a very high localization of the nuclei. In this respect, it is worthwhile to notice that the relative nuclear wavefunction reflects the presence of substantial correlation between the nuclei. This is manifested by the large power to which the internuclear coordinate is raised in equation (30). As discussed elsewhere [27], this strong correlation regime affecting the nuclear relative motion is a manifestation of Wigner crystallization. Quite to the contrary, the electrons, which are subjected to the simpler correlation function $(1 + r/2)$ show considerable delocalization

Comparison of the present model with the Hooke model for H_2, shows that in spite of the difference in the potential there is a substantial coincidence between the nucleus–pair probability distributions. Moreover, both models yield practically the same equilibrium distance. Let us remark that in contrast to the present model, for the Hookean model of H_2 it is not possible to obtain an exact analytic wavefunction.

Additionally, we have shown by explicit calculation of the electronic intracule densities and their associated momenta for the Hooke-Calogero model of H_2, that the electron dynamics is rather insensitive to the nature of the confining external potential, being it harmonic, like in the Hooke-Calogero model, or Coulombic. Even more, electron correlation appears to operate very similarly in both systems, as indicated by the remarkable similarity of the Coulomb holes of both systems.

The present exact analytic solution for the Hooke-Calogero model of H_2 may be useful in efforts to treat in a quantum mechanical manner the motion of nuclei. The reason is that the analytic expression given by equation (32) condenses in a very simple form the important quantum effects determining this motion. In turn, this opens the gate for exploring very compact approximations to describe the exact nucleus–pair probability in the real H_2 molecule. Such analytic approximations will allow us to derive density functionals for the nuclei in much the same manner as was done for electrons in a Hookean atom [43].

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