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Borromean binding in H_2 with Yukawa potential: A nonadiabatic quantum Monte Carlo study

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The stability of the ground state of the H_2^+ and H_2 systems, where nuclei and electrons interact through a Yukawa potential $e^{-\lambda r}/r$, has been studied for different values of the screening parameter λ using quantum Monte Carlo techniques. Nonadiabatic calculations using explicitly correlated trial wave functions were carried out, obtaining exact results within the statistical errors. H_2^+ and H_2 appear to be stable species for values of λ as large as 1.35 and 1.38 bohr^{-1}. So in the range $1.35 \leqslant \lambda \leqslant 1.38$ bohr^{-1} H_2 is stable, while all the possible fragments are unbound, that is, it shows Borromean binding.

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INTRODUCTION

A three-body system is called *Borromean* if it is bound, while all the two-body subsystems are unbound [1,2]. Phenomena related to the Borromean binding are the Efimov effect [3,4], for a vanishing two-body potential infinite weakly bound three-body states appear, and the Thomas collapse [5], for very small two-body binding the three-body energy becomes infinite upon reducing the potential range. Examples are known in nuclear physics [6] but not in atomic and molecular physics. Recently Richard has proposed the following generalization [1] to N-body systems: "A bound state is Borromean if there is no path to build it via a series of stable states by adding the constituents one by one." This means that in an N-body system all possible subsystems are unbound. An example of this behavior can be found in ^{3}He clusters. The $^3He_2$ molecule is unbound, however since the ^{3}He liquid is stable, there must exist a critical number of ^{3}He atoms bound to form the cluster ^3He_N. The exact value of N is still unknown. In an early investigation, Pandharipande *et al.* [7] using variational Monte Carlo (VMC) indicated that systems with more than 40 ^{3}He are bound, while 20 atoms are unable to ensure the binding. Recently this bound has been greatly improved by Guardiola and Navarro [8] who established at 35 a stricter upper bound to the minimum number of ^{3}He atoms needed to form a stable cluster. This cluster shows generalized Borromean behavior, since all 2-, 3-, and (N-1)-body subsystems are unbound.

Natural candidates to study the generalized Borromean binding are four-body systems. In particular, the stability of four-particle systems $M^+M^+m^-m^-$ interacting through a tunable screened Coulomb potential can be studied. Changing the interaction strength between particles allows investigating the range of stability of any combination of M^+ and m^- particles with respect to the relevant dissociation threshold.

Screened potentials are widespread in many different areas of physics and chemistry, being used in simple models to approximate many-body interactions. Among this set of potentials, one of the most important, both historically and practically, is the statically screened Coulomb potential, or Yukawa potential $Ze^{-\lambda r}/r$, where $Z=q_1q_2$, q_1 and q_2 being the charges of the interacting particles and r their distance. The screening parameter λ can vary from zero, for the unscreened case, to large values, allowing one to have different shieldings of the charge of the particles. This potential is quite often used to describe the shielding effects between charges due to thermal ionization in plasmas [9]. It has been applied also in condensed matter physics, mainly, to describe electronic properties in metals [10] and to model colloidal suspensions [11].

Besides the practical applications of the Yukawa potential to describe physical and chemical phenomena, there are many theoretical works primarily focused on the mathematical properties of this potential. In particular there have been attempts to find an accurate solution for the ground and excited states of simple systems, and therefore to determine the behavior of the energy upon variation of the screening parameter $E=E(\lambda)$, in order to understand for which value of λ the Yukawa potential is no longer able to support a bound state. At first, studies on the mathematical properties of the Yukawa potential were carried out on one-electron systems. Different approaches were used to build accurate approximations to the wave function and to evaluate the critical screening parameter: numerical integration [12], Padé approximants [13], and linear combination of simple functions [14] were among the most successful techniques. Then, the interest on this screened potential has been spreading over two-electron atomic systems, with a particular interest for the helium atom and the negative hydrogen ion [15–17]. The main goal of these works was to study the effect of the elec-

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tronic correlation on the stability of these systems upon variation of the screening parameter, in order to understand how and when the detachment of the electrons occurs. In the first attempts [17] to carry out these model calculations on H^-, the electron-electron repulsion term in the Hamiltonian was not screened, and the stability changed slightly upon variation of the screening parameter. Successively it was shown that for two-electron systems the introduction of screening in the electron-electron interaction increases the stability in comparison with the unscreened case. In particular for the negative hydrogen ion calculations [17,18] showed that the favored process is the simultaneous detachment of both the electrons,

$$\mathrm{H}^- \rightarrow \mathrm{H}^+ + 2e^-, \tag{1}$$

instead of the loss of only one electron, with production of neutral hydrogen:

$$\mathrm{H}^- \rightarrow \mathrm{H} + e^-. \tag{2}$$

The fact that the two electrons are ionized simultaneously as opposed to consecutively was shown to be true also for He and He^+ that lose their electrons for the same value of the screening constant [18].

Ugalde *et al.* [19] extended the study of systems interacting through a Yukawa potential to molecules. The interest was focused on the electronic and geometrical structures of the molecule H_2 for different values of the screening parameter. They used a full configuration interaction (CI) approach within the Born-Oppenheimer approximation in order to obtain the potential-energy surface.

Goy *et al.* [20] were the first to use the Yukawa potential to study weakly bound three-body systems with no bound subsystems. They assumed a potential $-gV$, V being the Yukawa potential with $\lambda = 1\ \mathrm{bohr}^{-1}$, and investigated the critical couplings g_3 and g_2 to bind three- and two-body systems and so the domain which produces Borromean binding.

The solutions for the above systems were fairly accurate, but the importance of the correlation energy increases as the screening parameter increases [19]. So to deal with this kind of problems we have to resort to methods that can deal with many-body correlation. Diffusion Monte Carlo [21] (DMC) techniques give exact results, within the statistical error, for systems whose wave function is positive everywhere. In this paper we report the results of nonadiabatic (NA) quantum Monte Carlo (QMC) calculations on the ground state of H_2^+ and H_2 molecules, upon variation of the screening parameter λ. In particular we are interested in calculating the range of stability upon variation of λ from the unscreened case $\lambda = 0\ \mathrm{bohr}^{-1}$ to large λ values, evaluating the critical parameter λ_c for which the systems are unbound. The choice of a NA approach is dictated by the need to get correct information for high values of λ. For very weakly bound systems it is not possible to follow the standard scheme, that is, to adopt the Born-Oppenheimer approximation and to correct for the zero-point energy evaluated within the harmonic approximation, owing to the anharmonicity of the fixed-nuclei potential.

HAMILTONIAN AND TRIAL WAVE-FUNCTION FORM

The Hamiltonian operator in atomic units describing a system of M nuclei and N electrons interacting through a Yukawa potential is

$$\hat{\mathrm{H}} = -\sum_{i=1}^{N+M} \frac{\nabla_i^2}{2m_i} + \sum_{i<j}^{N+M} \frac{q_i q_j}{r_{ij}} e^{-\lambda r_{ij}}, \tag{3}$$

where m_i are the masses of the particles.

The mass of the nuclei is set to 1836.1527 a.u. for NA calculations. The ground-state energy and eigenfunction of this Hamiltonian are parametrically dependent on the screening parameter. Increasing λ decreases the interaction energy between the particles, raising the total energy of the system. To discuss the range of stability of these systems, we define the critical screening parameter λ_c [22] as the value for which the energy of the system $E(\lambda) = \langle \hat{H}(\lambda) \rangle$ vanishes.

To obtain a variational estimate of the total energy, we approximate the trial wave function by the linear expansion [23,24],

$$\Psi_T = \hat{A}\hat{O}_{symm} \sum_{k=1} p_k \Phi_k \Theta_e \Theta_n, \tag{4}$$

where $\hat{A}$ is the antisymmetrization operator, $\hat{O}_{symm}$ is an operator used to fix the space symmetry, and Θ_e and Θ_n are the electronic and nuclear-spin eigenfunctions. The $\hat{O}_{symm}$ operators for H_2^+ and H_2 are, respectively,

$$\hat{O}_{symm,\mathrm{H}_2^+} = 1 + \hat{P}_{AB}, \tag{5}$$

$$\hat{O}_{symm,\mathrm{H}_2} = (1 + \hat{P}_{AB})(1 + \hat{P}_{12}), \tag{6}$$

where $\hat{P}_{AB}$ is the nuclear exchange operator and $\hat{P}_{12}$ in the electron exchange operator.

The space part of the wave function is

$$\Phi_k = \prod_{i<j} e^{U_{ijk}(r_{ij})}, \tag{7}$$

where the product runs over all the interparticle distances and the term $U_{ijk}(r_{ij})$ is the exponential of a Padé approximant,

$$U_{ijk}(r_{ij}) = \exp\left[\frac{a_{ijk} r_{ij} + b_{ijk} r_{ij}^2}{1 + c_{ijk} r_{ij}}\right]. \tag{8}$$

In the above equation a, b, and c are three variational parameters. The use of the complete Padé approximant instead of the more common Jastrow factor is motivated by the need to give maximum flexibility to the trial wave-function form.

The employed trial wave function depends only on the interparticle distances, so it is translationally invariant, and there is no need to subtract the kinetic energy of the center of mass from the total energy. The chosen trial wave-function form makes it impossible to compute analytically the matrix elements of the Hamiltonian, so we resort to the VMC method to accomplish this task. Since this and the other Monte Carlo methods employed in this work are well de-

TABLE I. Nonadiabatic ground-state energies of H_2^+.

λ (bohr^{-1})	E_{DMC} (hartree)	E_H (hartree)
0.0	−0.597136(3)	−0.499727
0.1	−0.503330(10)	−0.406789
0.7	−0.135561(13)	−0.071678
1.1899	−0.013489(13)	
1.20	−0.012287(15)	
1.25	−0.007201(10)	
1.29	−0.003989(14)	
1.33	−0.001597(12)	
1.34	−0.001190(11)	
1.35	−0.000750(10)	
1.36	−0.000400(10)	
1.365	−0.000280(16)	

TABLE II. Nonadiabatic ground-state energies of H_2.

λ (bohr^{-1})	E_{DMC} (hartree)	$2E_H$ (hartree)
0.0	−1.164032(9)	−0.999454
0.1	−0.976570(10)	−0.813578
0.7	−0.254304(9)	−0.143356
1.1899	−0.025926(20)	
1.25	−0.014465(15)	
1.29	−0.008541(22)	
1.33	−0.004060(38)	
1.35	−0.002343(36)	
1.36	−0.001544(30)	
1.365	−0.001317(30)	

scribed in the literature, we refer the reader to the various books and reviews available for the technical details [21,25,26]. All wave functions were optimized by minimizing the variance of the local energy, as described in the literature [25].

RESULTS

To optimize the parameters of the trial wave functions for each value of λ, we carried out VMC calculations using a one-term function as trial wave function and 10 000 random walkers. The same number of walkers and a time step of 0.01 hartree^{-1} for all the particles were used in NA-DMC simulations. In these simulations, to obtain comparable diffusion and sampling of the configuration space for particles of different masses, the time step should scale as $\sqrt{m}$. The adopted time step of 0.01 hartree^{-1} is a compromise, but it is rather large for electrons. A safe value for the energy could be calculated by extrapolation to zero time step, but NA-DMC simulations are computationally demanding, and a complete extrapolation to zero time step should be too expensive to be carried out for all the values of λ. So the accuracy of our NA results was assessed comparing the values for $\lambda = 0$ bohr^{-1}, computed with the 0.01 hartree^{-1} time step, with nearly exact literature results. For H_2^+ our energy −0.597 136(3) hartree is in agreement within the statistical error with the value −0.597 139 hartree computed by Bishop and Cheung [27]. For H_2 NA results were obtained by Traynor *et al.* [28] using Green's-function Monte Carlo [−1.164 024(9) hartree], and by Kinghorn and Adamowicz [29] (−1.164 025 023 2 hartree) using explicitly correlated Gaussians. Again our total energy −1.164 032(9) hartree is in statistical agreement with those practically exact values. In conclusion these comparisons support our choice for the time step for both the systems we studied. In any case we checked that the time step bias was negligible by running few more simulations with shorter time steps.

The results obtained by means of the NA-DMC simulations for various values of λ are shown in Table I for H_2^+ and in Table II for H_2, together with the nonadiabatic ground-state energy E_H for the hydrogen atom. The energies of the hydrogen atom with infinite nuclear mass E_∞, as a function of the screening parameter λ, were previously determined by Gomes *et al.* [22]. For $\lambda_{c,\infty}$ they predicted a value 1.190 612 27(4) bohr^{-1}: from this value the finite-mass critical screening parameter $\lambda_{c,M} = 1.1899$ bohr^{-1} is evaluated according to the Appendix. The energies of the hydrogen atom with finite nuclear mass were computed by analytical calculations with a linear expansion of 19 exponential functions, i.e.,

$$\Psi(r) = \sum_{i}^{19} c_i e^{-k_i r}, \tag{9}$$

optimizing both linear and nonlinear parameters.

Stability of H_2^+

We extended previously published calculations [30] to larger values of λ to better compare the relative stability of H_2 against this system. We used only one term in the trial wave functions for the NA simulations, since DMC can give the exact energy as the space parts of the electronic and nuclear functions are positive everywhere.

From Table I it emerges that for H_2^+

$$\begin{gathered} E_{H_2^+}(\lambda) < E_H(\lambda), \\ \lambda_c^{H_2^+} > \lambda_c^{H}, \end{gathered} \tag{10}$$

since for $\lambda = 1.2$ bohr^{-1} H_2^+ is bound, while H is not. In the range where the hydrogenlike atoms are stable, for $\lambda < \lambda_c^H$, H plus H^+ give the relevant threshold, and this means that H_2^+ is stable against the dissociation

$$H_2^+ \rightarrow H + H^+. \tag{11}$$

Instead, for $\lambda_c^H \leqslant \lambda \leqslant \lambda_c^{H_2^+}$, the system is stable against the dissociation

$$H_2^+ \rightarrow 2H^+ + e^-, \tag{12}$$

because in this range of λ values the hydrogenlike atom is not bound. A few interesting conclusions can be drawn from

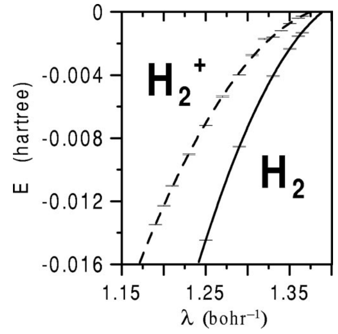

FIG. 1. NA-DMC energies as a function of λ for H_2^+ and H_2.

our results: since H_2^+ is stable even when H is not, H_2^+ is a Borromean system [20], a three-body system with two of the two-body potentials attractive and one repulsive. Moreover, if one compares the value of −0.000 000 103 hartree for the energy of the hydrogenlike system with $\lambda = 1.19\ \text{bohr}^{-1}$ as computed by Vrscay [13], with the energy value −0.012 278(15) of H_2^+ with $\lambda = 1.2\ \text{bohr}^{-1}$ shown in Table I, it strikes that the total energy lowers by a factor of 10^5 when a proton is added to the hydrogenlike atom.

Although it is hard to properly assess the different contributions to this effect that come from each part of the Hamiltonian operator, it appears strictly dependent on the simultaneous action of the two attractive contributions due to the nuclei on the electron, since it is present also in calculations performed within the Born-Oppenheimer approximation. It remains to understand how much of this effect is due to the symmetry of the Hamiltonian itself, i.e., same mass for the positive particles and same screening constant λ in the potential, and how much the ground-state energy might change upon variation of these physical parameters.

We computed the mean value of the bond distance R_0 by the mixed estimator: a correct evaluation of this property should require a forward walking algorithm [21], so our values are only a first estimate of R_0. Upon increasing λ, the bond is weakened and R_0 increases; the largest value just before dissociation is 3.60(1)bohr.

Stability of H_2

Our total energies, shown in Table II, are consistently higher than the values obtained by means of full CI calculations after correction for the zero-point vibrational energy [19]. This fact stresses the importance of NA calculations for a correct prediction of the stability of this system. For easy comparison with the results for H_2^+ data are plotted in Fig. 1. The values of the critical parameters λ_c for H_2 and H_2^+, together with the literature data for H and H^- corrected for finite mass, are collected in Table III. The physical picture of H_2 given by the NA results is the same as for H_2^+. For all the values of the screening parameter λ we explored, the following relations hold:

$$E_{H_2}(\lambda) < E_{H_2^+}(\lambda),$$

$$E_{H_2}(\lambda) < 2E_H(\lambda), \qquad (13)$$

$$\lambda_c^{H_2} > \lambda_c^{H_2^+} > \lambda_c^{H}.$$

TABLE III. Screening parameter λ_c critical values.

System	λ_c (bohr^{-1})
H	1.1899
H^-	1.1899
H_2^+	1.373(4)
H_2	1.385(7)

For values of the screening parameter $\lambda \geqslant \lambda_c^H$, as shown in Fig. 1, H_2 is stable against the dissociations

$$H_2 \rightarrow 2H,$$

$$H_2 \rightarrow H_2^+ + e^-, \qquad (14)$$

while for $\lambda_c^{H_2^+} \leqslant \lambda \leqslant \lambda_c^{H_2}$ H_2 is stable against the only possible dissociation $H_2 \rightarrow H_2^+ + e^-$. The other possible dissociation path $H_2 \rightarrow H^- + H^+$ is excluded as H^- has the same λ_c as H. So in this range of λ there is no path to build H_2 via a series of stable states by adding the constituents one by one, namely, H_2 shows Borromean binding in the generalized sense.

Our mean bond distances are in good agreement with the values found in literature [19] for all the λ values. Our results, in agreement with the full CI calculations [19], show that R_e increases upon increasing the parameter λ, even if the lengthening of the bond is less than in H_2^+.

CONCLUSIONS

In this work we have explored the stability range of the two molecular systems H_2^+ and H_2, whose particles interact through the Yukawa potential, varying the screening parameter λ. These two molecular systems are bound in a larger range of λ in comparison to the atomic systems H and H^-. In particular H_2 is stable for larger values of λ than H_2^+. H and H^- show the same critical value of the screening constant λ_c, so H^- loses both electrons simultaneously and does not show Borromean binding. For $\lambda_c > 1.375\ \text{bohr}^{-1}$ H_2 is the only stable system and so is in a Borromean state. Since the screening parameter is a function of both the electron density and the electron temperature, a particular value of λ corresponds to a range of plasma conditions. Although the Yukawa model potential may not always be appropriate to model a real plasma, in particular for values of the screening parameter near the critical one, these results show that it has very interesting mathematical properties, being able to support generalized Borromean binding.

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APPENDIX: ESTIMATE OF THE CRITICAL SCREENING PARAMETER FOR THE HYDROGEN ATOM WITH FINITE NUCLEAR MASS *M*

The finite-mass Hamiltonian operator for the hydrogen atom is

$$\hat{H}(\lambda) = -\frac{1}{2\mu}\nabla^2 - \frac{e^{-\lambda r}}{r}, \tag{A1}$$

where $\mu = M/(M+1)$ is the reduced mass. If $\lambda = \lambda_{c,M}$, then $\langle \hat{\mathrm{H}}(\lambda_{c,M})\rangle = 0$. Let us scale r as $r \to ar$; then

$$\hat{\mathrm{H}}(\lambda_{c,M}) = -\frac{a^2}{2\mu}\nabla^2 - a\frac{e^{-\lambda_{c,M} r/a}}{r}. \tag{A2}$$

Multiplying by μ/a^2 and then setting $\mu = a$, we can write

$$\hat{\mathrm{H}}(\lambda_{c,M}) = -\frac{1}{2}\nabla^2 - \frac{e^{-\lambda_{c,M} r/\mu}}{r} = \hat{\mathrm{H}}(\lambda_{c,\infty}), \tag{A3}$$

where $\hat{\mathrm{H}}(\lambda_{c,\infty})$ is the infinite-mass Hamiltonian operator with critical screening parameter $\lambda_{c,\infty} = \lambda_{c,M}/\mu$.

Using the best estimate of $\lambda_{c,\infty} = 1.190\,612\,27(4)$ bohr^{-1} [22], we obtain $\lambda_{c,M} = 1.189\,96$ bohr^{-1}.

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