

# Atomic and molecular bound ground states of the Yukawa potential

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The variational self-consistent field molecular-orbital method is used to compute both atomic and molecular full configuration interaction (FCI) energies of the hydrogen anion and the hydrogen molecule, for the Yukawa potential. The spin orbitals have been expanded as linear combinations of Gaussian basis functions, for which complete analytical formulas for all the required basic integrals are available. Both the ionization potential of the hydrogen anion and the behavior of the molecular properties of the hydrogen molecule have been analyzed in detail with extensive basis sets at the FCI level of theory. Finally, the growing importance of the electron correlation energy as the screening parameter increases has been demonstrated clearly by our calculations. [S1050-2947(97)01208-0]

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## I. INTRODUCTION

Screened Coulomb potentials have important applications in many areas of physics. One of the simplest forms of statically screened Coulomb potentials, namely, the Yukawa potential, may be used to approximate the effects of the screening of nuclear charges by plasmas [1]. In this context, the problem of finding the energy levels of a hydrogen atom in an electron gas has received considerable attention in the past [2–4].

Recently, earlier work was revised and complemented with accurate numerical calculations. Excellent results for a wide range of the screening parameter have been reported for the  $1s$ ,  $2s$ , and  $2p$  states of the hydrogen atom [5], using the Rayleigh-Schdinger perturbation expansion of the energy. Also, it was recently shown that energy variational calculations [6,7], with a Slater-type basis function set, can yield very accurate results for the hydrogen atom. Particularly, for states higher in energy than  $2p$ , this method produces the most accurate results published to date.

For expanding the studies of polyelectronic atoms and/or molecules with statically screened Coulomb potentials, it is encouraging that the energy variational procedure with the expansion of the spatial wave function as a linear combination of simple functions is so efficient, for this is essentially the method used in current atomic and/or molecular electronic structure calculations [8]. In particular, for molecules, the self-consistent field molecular-orbital (SCF-MO) theory is widely used [9]. Customarily the molecular orbitals are built as a linear combination of the atomic orbitals expanded in terms of Gaussian basis functions, instead of Slater-type basis functions. The reason for this is that for the former all required integrals can be carried out analytically [10]. Likewise, newly developed density-functional theory based programs also make successful use of Gaussian basis set expansions [11].

It has been recently shown [12] that the molecular integrals required to solve the self-consistent field molecular orbital problem for the Yukawa potential can be worked out analytically in terms of the generalized Cartesian Gaussian basis sets. This allows for the efficient implementation of the SCF-MO theory and hence for the analysis of the structure of

atoms and molecules with the Yukawa statically screened interaction potentials. In this paper we report results from calculations of the bound states of the Yukawa potential for the hydrogen anion and the hydrogen molecule, two interesting two-electron systems.

## II. METHOD

For our purposes we are interested in finding a set of spin orbitals  $\{\chi_a\}$  such that a full configuration interaction (FCI) wave function  $|\Psi\rangle$ , built with them is the best possible approximation of the ground state of a system with  $N$  electrons and  $M$  nuclei, of charge  $Z_A$ . The electronic Hamiltonian describing this system is

$$\hat{H} = \hat{T} + \hat{V}, \quad (1)$$

$$\hat{T} = \sum_{i=1}^N -\nabla_i^2/2, \quad (2)$$

$$\hat{V} = -\sum_{A=1}^M \sum_{i=1}^N \frac{Z_A e^{-\lambda r_{iA}}}{r_{iA}} + \sum_{i>j}^N \frac{e^{-\lambda r_{ij}}}{r_{ij}} + \sum_{A>B}^M \frac{Z_A Z_B e^{-\lambda R_{AB}}}{R_{AB}}, \quad (3)$$

where  $\lambda$  is the screening parameter,  $r_{iA}$  is the distance between electron  $i$  and nucleus  $A$ ,  $r_{ij}$  is the distance between electrons  $i$  and  $j$ , and  $R_{AB}$  is the distance between nuclei  $A$  and  $B$ . The  $\chi_a$  spin orbitals will be expanded in terms of Gaussian basis set functions. Solving the FCI problem is tedious and difficult but feasible for few-electron systems with the aid of modern electronic structure procedures [8]. All calculations presented in this paper have been carried out with a locally modified version of the GAMESS suite of programs [13] which has been interfaced with our basic Yukawa molecular integrals package [12].

An internal check for the quality of the wave function is provided by the quantum mechanical virial theorem [14]

$$\left\langle \Psi \left| \sum_i^N \left( x_i \frac{\delta \hat{V}}{\delta x_i} + y_i \frac{\delta \hat{V}}{\delta y_i} + z_i \frac{\delta \hat{V}}{\delta z_i} \right) \right| \Psi \right\rangle = 2 \langle \Psi | \hat{T} | \Psi \rangle, \quad (4)$$

which bound stationary states must satisfy [14]. Therefore, substituting Eqs. (2) and (3) into Eq. (4), we obtain

$$\begin{aligned}
2\langle\hat{T}\rangle = & -\langle\hat{V}\rangle + \lambda \left[ \sum_A Z_A \left\langle \sum_i e^{-\lambda r_{iA}} \right\rangle \right. \\
& \left. - \left\langle \sum_{i>j} e^{-\lambda r_{ij}} \right\rangle - \left\langle \sum_{A>B} Z_A Z_B e^{-\lambda R_{AB}} \right\rangle \right] \\
& - \sum_{A>B} R_{AB} \left( \frac{\delta E}{\delta R_{AB}} \right), \quad (5)
\end{aligned}$$

where  $E$  is the total energy, and  $\langle\hat{O}\rangle$  stands for the quantum-mechanical average of the operator  $\hat{O}$  over the electron coordinates. For atoms, the third term in the bracket and the last term of the right-hand side of Eq. (5) disappear. We have checked that all the bound stationary states reported in this paper satisfy Eq. (5).

### III. RESULTS AND DISCUSSION

The analytical exponential potential of Yukawa has been found to be a feasible representation of the electric interaction between nuclei and electrons for some plasma environments [7]. Therefore, previous calculations of the energy levels on one-electron systems interacting through the Yukawa potential [2–6] have been extended to two-electron systems [7,15–17]. In particular, attention has been recently drawn to the stability of the ground state of the  $\text{H}^-$  [7,15,16] and the ground [16,17] and excited states of He [17]. Also, the prediction of the emission oscillator strength of the dipole-allowed transitions of the helium atom, as a function of the screening parameter, has been investigated [17]. However, some of the previous calculations [7] have been carried out within the pair function many-body perturbation theory [18], whose performance has been found to deteriorate noticeably as the screening parameter increases [17]. In recent studies on the detachment energy for  $\text{H}^-$  [15], and on the ground [16,17] and excited states [17] of He, it has been demonstrated that both variational wave functions which include the interelectronic distance [15,16] and FCI-type wave functions [17] are uniformly effective within a broad range of  $\lambda$  values.

#### A. Stability of $\text{H}^-$

The hydrogen anion represents a challenging problem for the electronic structure calculations, for it is well known that its stability is highly dependent upon the treatment of the electron correlation. Therefore, taking this effect into account properly is mandatory for this system. We have calculated the FCI energy of  $\text{H}^-$  with the  $11s5p5d$  uncontracted Gaussian basis set built from the  $9s3p1d$  uncontracted basis set of Siegbhan and Liu [19], augmented by two sets of  $s$ - and  $p$ -type and four sets of  $d$ -type functions. The exponents of the added functions were chosen to form an even tempered set with a ratio 3.0 with respect to the most diffuse function of each type.

The total energy for the unscreened ( $\lambda=0$ ) case is  $-0.527\,388$  hartree. Hence the basis set incompleteness, with respect to the *exact* energy of Hart and Herzberg [20], is of only 0.25 m hartree, and its stability, with respect to the

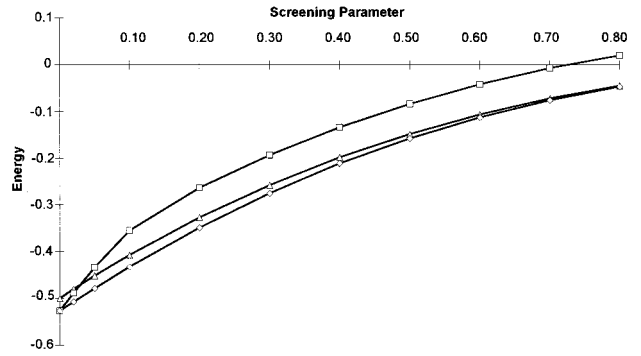


FIG. 1. Energies (in hartree) of the hydrogen atom ( $\Delta$ ) and the hydrogen anion with both the nucleus-electron and the interelectronic interactions screened ( $\diamond$ ) and with only the nucleus-electron interaction screened ( $\square$ ), as a function of the screening parameter.

hydrogen atom, is 27.4 m hartree. As shown in Fig. 1, this stability decreases very slowly as the screening parameter increases. Thus, for  $\lambda=0.9$ ,  $\text{H}^-$ ,  $-0.024\,415$  hartree, is still more stable than H,  $-0.024\,313$  hartree. This suggests, as found earlier by Winkler [15], that the two electrons of  $\text{H}^-$  detach simultaneously as a consequence of the screening.

In calculations using the pair-function many-body perturbation theory, Wang and Winkler [7] reported that  $\text{H}^-$  is unbounded for  $\lambda \geq 0.029$  a.u. However, they screened only the nucleus-electron interaction, while, in our calculations, both the nucleus-electron and the electron-electron interactions have been screened. Indeed, we have repeated our calculations with the electron-electron interaction unscreened and been able to reproduce the essential characteristics of their results. In addition, we have extended their analysis over a wider range of  $\lambda$  values. Also seen in Fig. 1, it is found that for  $\lambda \geq 0.3$  a.u. the energy difference between  $\text{H}^-$ , with the electron-electron interaction unscreened, and H remains constant, being H 64.7 m hartree more stable than  $\text{H}^-$ .

#### B. Hydrogen molecule

The convergence of the energy with respect to the increase of the basis set size in known to be slow for the unscreened of the hydrogen molecule [21]. Therefore, it is important to check whether this behavior is also found in the case of the screened molecule.

Consider the unscreened  $\text{H}_2$  in its ground  $^1\Sigma_g^+$  electronic state. The  $(9s/4s)$  contracted basis set of Siegbhan and Liu [19] yields a FCI energy of  $-1.154\,346$  hartree. Thus its basis set incompleteness, with respect to the *exact* value of Kolos and Wolniewicz [22], is 20.0 m hartree. This basis set has been augmented by adding the following polarization function sets:  $1p$ ,  $2p$ ,  $3p1d$ , and  $3p2d$ , whose exponents have been given earlier [21].

We have carried out geometry optimizations with each of the above-mentioned basis sets at the FCI level of theory, for various selected values of the screening parameter. The results indicate that the convergence of the screened energy, with respect to the increase of the basis set size, is not worse than that of the unscreened case ( $\lambda=0$ ). Figure 2 shows the energy lowering achieved by each of the augmented basis

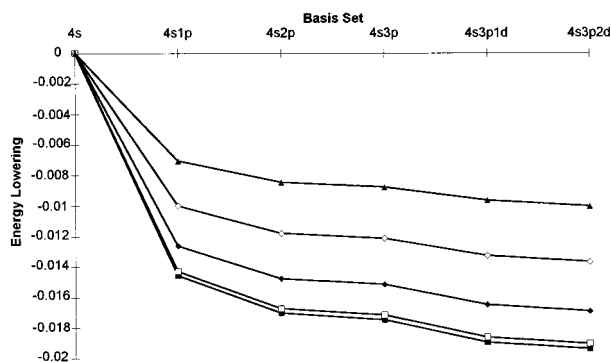


FIG. 2. Energy lowering (in hartree) of  $H_2$  due to the increase of the basis set size with respect to the base level energy obtained with the  $4s$  contracted basis set, for selected values of the screening parameter. Bottom curve:  $\lambda=0$ ; then  $\lambda=0.1$ ,  $\lambda=0.3$ ,  $\lambda=0.5$ , and  $\lambda=0.7$ , respectively.

sets with respect to the base level ( $9s/4s$ ) contracted basis set, for some selected values of  $\lambda$ . Inspection of the patterns unveiled by Fig. 2 suggests that the convergence of the energy is slow for all the basis sets investigated, irrespective of the value of the screening parameter. Nevertheless, it is observed that the behavior for values of  $\lambda$  greater than zero parallels closely that of  $\lambda=0$ .

In the case of the convergence of the optimum bond length  $R_e$ , the convergence with respect to the basis set size is also slow. As shown in Fig. 3, addition of one  $p$  set of polarization functions to ( $9s/4s$ ) yields a remarkable shrinkage of the optimum bond length. Further addition of more  $p$  or  $d$  sets has only a minor effect on  $R_e$ .

Finally, we have calculated the FCI dissociation energy  $D_e$  of the hydrogen molecule, including the zero-point vibrational energy correction, with our largest basis sets, for various values of  $\lambda$ . All results are collected in Table I. It is immediately observed that as the screening parameter increases, the optimum bond length increases, and that the molecule becomes less bound with respect to two screened hydrogen atoms. This indicates that the nucleus-electron attractive interaction is screened more effectively than the repulsive electron-electron and nucleus-nucleus interactions. Interestingly, the absolute electron correlation energy decreases as the screening increases. However, closer inspection of the data shown in Table I, reveals that, as a percentage of the total FCI energy, the electron correlation energy actually grows as  $\lambda$  increases, which is suggestive of the

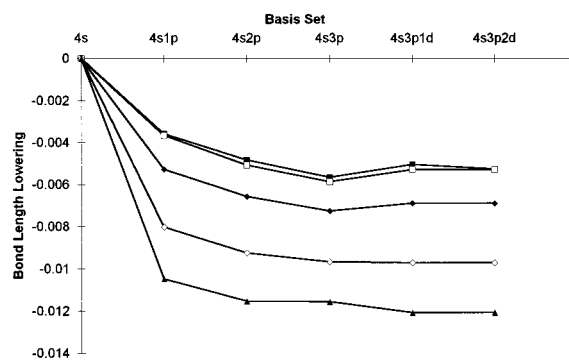


FIG. 3. Shrinking of the optimum bond length (in Å) of the  $H_2$  due to the increase of the basis set size with respect to the base level energy obtained with the  $4s$  contracted basis set, for selected values of the screening parameter. Top curve:  $\lambda=0$ , then  $\lambda=0.1$ ,  $\lambda=0.3$ ,  $\lambda=0.5$  and  $\lambda=0.7$ , respectively.

growing importance of the electron correlation effects as the screening parameter increases.

#### IV. CONCLUSIONS

We have calculated the full configuration-interaction energies of the hydrogen anion and the hydrogen molecule when their electrons and nuclei interact through the Yukawa potential. The spin orbitals have been expanded in terms of Gaussian basis functions, for which fully analytical formulas for the molecular integrals involved in the solution of the self-consistent field problem are available. Also, the quality of the wave functions obtained has been verified with the aid of the quantum-mechanical virial theorem.

Our calculations demonstrate that the behavior of both the convergence and the stability of the calculated energies, with respect to increasing basis set size, is essentially equal to that of the unscreened case. Therefore, all the skill and knowledge that have become available on electron correlation and Gaussian basis sets can be exercised with screened atoms and molecules.

It has been found that the importance of the correlation energy increases as the screening parameter increases. Hence electron correlation effects should be accounted for properly to arrive at meaningful conclusions for screened atoms and molecules. We have been able to obtain accurate energy differences between the neutral and anionic hydrogen atom. This information, augmented by the analysis of the line broadening, can be relevant for diagnostics of hydrogen plasmas.

TABLE I. Optimized bond length  $R_e$  in Å, FCI energy of  $H_2$ ,  $E_{\text{FCI}}$ ; energy of H,  $E_H$ , in hartree, dissociation energy  $D_e$  and zero-point vibrational energy ZPVE of  $H_2$ , in kcal/mol; electron correlation of  $H_2$ , in hartree, and percentage of electron correlation energy in the FCI energy of  $H_2$ . Results were obtained with the contracted  $4s3p2d$  Gaussian basis set.

$\lambda$	$R_e$	$E_{\text{FCI}}$	$E_H$	$D_e$	ZPVE	$E_{\text{corr.}}$	% corr.
0.00	0.742	-1.17 3752	-0.499 998	107.99	1.04	0.040 169	3.42
0.10	0.745	-0.986 208	-0.407 056	106.96	1.03	0.039 512	4.01
0.30	0.765	-0.676 369	-0.257 624	100.14	0.96	0.035 385	5.23
0.50	0.802	-0.438 651	-0.147 949	88.72	0.86	0.029 160	6.65
0.70	0.856	-0.260 717	-0.070 711	74.14	0.72	0.022 072	8.47

The nuclear-electron attractive interaction is screened more efficiently by the Yukawa potential than the interelectronic and the internuclear repulsive interactions. Consequently, the optimum bond length and the dissociation energy of the hydrogen molecule increase and decrease, respectively, as the screening parameter increases. Additionally, it is worth noting that the rate of change of both the optimum bond length and the dissociation energy is small for

small values of the screening parameter, and large for larger values of the screening parameter.

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