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Hubbard Hamiltonian for the hydrogen molecule

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An attempt is made to derive the parameters of the Hubbard Hamiltonian for the hydrogen molecule from state-of-the-art quantum chemistry calculations of the ground and excited states of the neutral and singly ionized molecules (eight states altogether). Calculations are carried out for interatomic distances in the range 0.6–4.3 Å. The results clearly indicate that the on-site repulsion U is not enough to fit the *ab initio* energies and that it is necessary to incorporate the intersite repulsion (usually referred to as J). If J is ignored, the fitted on-site repulsion approaches the atomic value very slowly as the interatomic distance is increased, a clearly unphysical behavior. For finite J and at the equilibrium interatomic distance, the energies of the eight states mentioned above are reasonably fitted with an atomic orbital energy $\epsilon_0 \approx -24.6$ eV, Coulomb interaction parameters $U \approx 11.6$ eV and $J \approx 8.9$ eV, and a hopping integral $t \approx 7.9$ eV.

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I. INTRODUCTION

The Hubbard Hamiltonian[1] is one of the main tools used by condensed matter physicists to investigate effects derived from the electron-electron interaction. In particular it is able to catch the main physics of phenomena as elusive as the metal-insulator transition[2,3] and the Kondo effect.[4,5] In the 1990s, it was widely used to investigate the nature of the pairing interaction in high-temperature superconductors.[6–12] More recently, the Hubbard Hamiltonian has been used to investigate the effects of the electron-electron interaction on transport through nanostructures and molecules[13–15] and the Kondo resonance in quantum dots[16,17] and in molecules[18–20] or atoms[21] adsorbed on metallic surfaces.

The simplest version of the Hubbard Hamiltonian includes a single atomic orbital on each site, hopping between nearest-neighbor orbitals, and the on-site repulsion; intersite interactions are neglected. Investigating the physics of some systems has required the incorporation of more atomic orbitals and electron-electron interactions between orbitals on the same or on different sites (or atoms).[7,9,22] More recently, it has been suggested that the hopping integral may significantly depend on the charge state.[23] It is worth noting that although the version of the Hubbard Hamiltonian which incorporates intersite electron-electron interactions is currently known in the physics literature as the "extended Hubbard model," it was introduced long before by Pariser and Parr.[24] Actually, the Hubbard model is just a particular case of the semiempirical model Hamiltonian introduced in Ref. 24. One of the key questions of any model Hamiltonian is the choice of the set of parameters that have to be used to describe a particular physical system. This issue was carefully addressed in Ref. 9 where a technique was proposed to derive the parameters of an extended Hubbard model for the cuprate La_2CuO_4. Many other works have focused on this important issue.[10–12]

Being involved in derivations of model Hamiltonian parameters similar to those mentioned above, we realized that the simplest case to which the Hubbard Hamiltonian could be applied—namely, the hydrogen molecule[25]—had not been discussed in detail. The purpose of this work is to present such a discussion. As the Hubbard Hamiltonian was devised to describe both charge and spin excitations, we made an attempt of fitting the model parameters to give the *ab initio* energies of the ground and excited states of the neutral and singly ionized molecules. Several interesting results emerge from this analysis. In particular, our results indicate that a fitting that only includes the on-site Coulomb repulsion parameter U (actually the Hubbard parameter) leads to unphysical results. For instance a fitting of the ground and excited states of the neutral molecule gives a U that approaches the atomic value, upon increasing the interatomic distance, very slowly. In addition, a poor fitting is obtained when the states of the singly ionized molecule are also included. Incorporating the intersite Coulomb repulsion J eliminates up to a great extent those flaws, allowing a reasonable fit of the *ab initio* energies of the ground and excited states of the neutral and singly ionized molecules for interatomic distances over the range 0.6–4.3 Å.

II. METHODS

A. *Ab initio* calculations

We have carried out state-of-the-art quantum chemistry calculations of the energies of the ground and excited states of neutral and singly ionized hydrogen molecules (H_2, H_2^-, and H_2^+) as a function of the interatomic distance (potential

TABLE I. *Ab initio* energies $E(\mathrm{AI})$ of the ground and excited states of the neutral (E_i^0, $i=1,\ldots,4$) and singly ionized ($E_i^{\pm}$, $i=1,2$) hydrogen molecules at the equilibrium distance (0.7412 Å). Results obtained in this work (second column) and those obtained by other authors by means of large sets of functions (third column) are reported. The energies obtained from several fittings of the Hubbard Hamiltonian $E(H)$ are also shown, along with the resulting parameters (see text) and the respective relative standard deviation σ (see text). The ion-ion interaction (0.71395 a.u.) has been subtracted from all *ab initio* energies. All energies and parameters are given in atomic units (a.u.).

State	$E(\mathrm{AI})$	$E(\mathrm{AI})$	$E(H)$	$E(H)$	$E(H)$
E_1^0 ($X\,^1\Sigma_g$)	−1.8971	−1.8884[a]	−1.982	−1.8857	−2.0181
E_2^0 ($^3\Sigma_u$)	−1.4919	−1.4981[a]	−1.440	−1.6050	−1.4830
E_3^0 ($^1\Sigma_u$)	−1.4263	−1.4177[b]	−1.379	−1.0833	−1.3834
E_4^0 ($^1\Sigma_g$)	−0.8207		−0.8365	−0.8026	−0.8483
E_1^+ ($X\,^2\Sigma_g$)	−1.2836	−1.2843[c]		−1.0398	−1.1960
E_2^+ ($^2\Sigma_u$)	−0.8161			0.5652	−0.6132
E_1^- ($X\,^2\Sigma_u$)	−1.8346			−2.1230	−1.9272
E_2^- ($^2\Sigma_g$)	−1.4350			−1.6485	−1.3444
ϵ_0			−0.7198	−0.8025	−0.9046
t			0.2859	0.2373	0.2914
U			0.0611	0.5218	0.4257
J			0.0	0.0	0.3261
σ			0.034	0.138	0.047

[a] See Ref. 35.
[b] See Ref. 36.
[c] See Ref. 37.

energy curves). Only those excited states that can be reached with a minimal basis set have been investigated. These include the following excitations of the ground states: one double and two single excitations in neutral hydrogen and a single excitation in each of the singly ionized states. The basis function set used in all calculations was the aug-cc-pVTZ,[26] which guarantees a precision of 1 mhartree in energy. Since the calculation involves excited states of the same symmetry as the ground state, we are forced to use multideterminantal wave functions. Thus, multiconfiguration self-consistent-field (MCSCF) wave functions[27] on the active space of two molecular orbitals have been used, generating, subsequently, the fully optimized set in the reaction space [complete active space SCF (CASSCF); see Ref. 28]. Given the characteristics of the systems investigated here, the CASSCF wave function will be, in some cases, a restricted open-shell Hartree-Fock (ROHF) wave function.

As the MCSCF wave function incorporates only part of the correlation energy, it is essential to find a way to compensate for this deficit. We have chosen the method proposed by Colle and Salvetti[29] which is the basis of the density functional proposed by Lee, Yang, and Parr.[30] As the method depends on the two-body density matrix, it is greatly sensitive to the particular wave function used in the calculations. Notwithstanding, it provides a correlation energy that compensates the deficit of the multiconfiguration wave functions to a greater extent than other density functionals.[31,32]

All calculations were done using a modified version of GAMESS,[33] which evaluates the correlation energy by numerical integration as a post-SCF procedure, except the one-electron system that was treated with GAUSSIAN 03.[34]

The numerical results obtained in these work for the energies of the states $X\,^2\Sigma_g$ and $^2\Sigma_u$ of H_2^+, $X\,^1\Sigma_g$, $^3\Sigma_u$, $^1\Sigma_u$, and $^1\Sigma_g$ of H_2, and $X\,^2\Sigma_u$ and $^2\Sigma_g$ of H_2^-, at the equilibrium distance, are reported in Table I, along with those available in the literature. In addition, the energies of those states versus the H-H distance are plotted in Fig. 1. The results for the ground state and the first excited state of neutral H_2 agree very satisfactorily with those reported by Kolos and Wolniewicz,[35] while those for the second excited state fairly agree with the result obtained by Kolos and Roothaan.[36] In

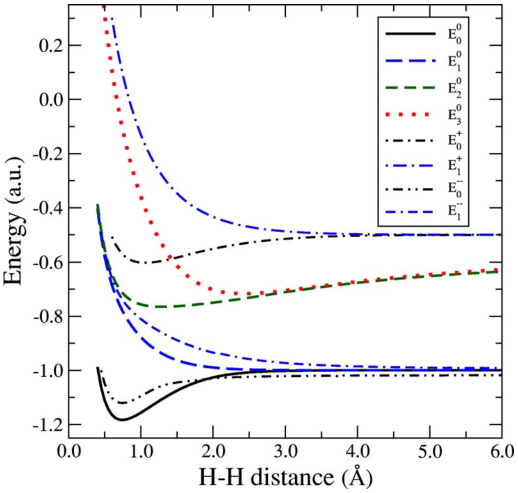

FIG. 1. (Color online) *Ab initio* energies (thick curves) of the ground and excited states of the neutral and singly ionized hydrogen molecules versus the H-H distance.

both cases,[35,36] wave functions which depend on interelectronic distance were included. As regards H_2^+ and H_2^-, we address the reader to Refs. 37, 38, and 39–42, respectively. The case of the negatively charged ion deserves some additional comments. Our results show trends similar to those reported in works previously published by different groups.[39–42] It is first noted that although the potential curve shows a minimum at a H-H distance similar to that in neutral hydrogen (see Fig. 1), the energy of the ground state of the negative ion is higher than that of the neutral molecule. This indicates that the negatively charged hydrogen molecule is not stable relative to autoionization into neutral hydrogen and an electron at infinity.[39] At large distances, however, our results indicate that the ion is stable, in agreement with previous studies (see, for instance, Ref. 41).

B. Hubbard Hamiltonian

The Hubbard-like model Hamiltonian used to describe the hydrogen molecule contains a noninteracting part H_0 and a term that incorporates the electron-electron interactions H_I:

$$\hat{H} = \hat{H}_0 + \hat{H}_I. \tag{1}$$

The noninteracting term is written as

$$\hat{H}_0 = \epsilon_0 \sum_{i=1,2;\sigma} c^\dagger_{i\sigma} c_{i\sigma} + t \sum_{i\neq j;\sigma} c^\dagger_{i\sigma} c_{j\sigma}, \tag{2}$$

where the operator $c^\dagger_{i\sigma}$ creates an electron at site i with spin σ, ϵ_0 is the energy of the atomic orbital, and t is the hopping between sites (kinetic energy). The interacting part is in turn given by

$$\hat{H}_I = U \sum_{i=1,2;\sigma} n_{i\uparrow} n_{i\downarrow} + J \sum_{i\neq j;\sigma,\sigma'} n_{i\sigma} n_{j\sigma'}, \tag{3}$$

where U is the on-site Coulomb repulsion (Hubbard term) and J is the intersite Coulomb repulsion, usually included in the extended version of the Hubbard Hamiltonian,[9,22] while the density operator is

$$n_{i\sigma} = c^\dagger_{i\sigma} c_{i\sigma}. \tag{4}$$

There is the possibility of differentiating between intersite Coulomb repulsions among electrons with either the same or different spins. However, we have explored such a possibility without significant improvements in the fittings.

Then, the energies of the ground and excited states of neutral hydrogen, E_i^0, $i=1,\ldots,4$, are

$$E_1^0 = 2\epsilon_0 + 0.5(U+J) - 0.5(U-J)\sqrt{1+\left(\frac{16t}{U-J}\right)^2}, \tag{5}$$

$$E_2^0 = 2\epsilon_0 + J, \tag{6}$$

$$E_3^0 = 2\epsilon_0 + U, \tag{7}$$

$$E_1^0 = 2\epsilon_0 + 0.5(U+J) + 0.5(U-J)\sqrt{1+\left(\frac{16t}{U-J}\right)^2}. \tag{8}$$

The equations for the ground state and the highest excited state have been written to make clearer its behavior at large interatomic distances and taking account of the fact that U is usually larger than J for all interatomic distances. For instance, the limits of the four states at large distances—namely, $2\epsilon_0+J$ (ground and first excited states) and $2\epsilon_0+U$ (the remaining excited states)—are in this way evident.

On the other hand, the energies for the ground and excited states of the positively (E_i^+) and negatively (E_i^-) charged molecules are

$$E_1^+ = \epsilon_0 - t, \tag{9}$$

$$E_2^+ = \epsilon_0 + t, \tag{10}$$

$$E_1^- = 3\epsilon_0 - t + U + 2J, \tag{11}$$

$$E_2^- = 3\epsilon_0 + t + U + 2J. \tag{12}$$

The fitting of the parameters of the model Hamiltonian was carried out by minimizing the standard deviation

$$\sigma = \sqrt{\frac{1}{N}\sum_{i=1,\ldots,N}\left[\frac{E_i(H)-E_i(\mathrm{AI})}{E_i(\mathrm{AI})}\right]^2}, \tag{13}$$

where $E_i(\mathrm{AI})$ and $E_i(H)$ are the *ab initio* and the Hubbard Hamiltonian energies of the N states included in a particular fitting. This choice is based upon the fact that the relative error is a less biased magnitude than the absolute error. The ion-ion repulsive energy was subtracted from all the *ab initio* energies, as this contribution is not included in the Hamiltonian of Eq. (1).

In order to determine the parameters of the Hubbard model in the atomic limit (dissociated molecule) we have also calculated the energy of neutral and negatively ionized atomic hydrogen. *Ab initio* calculations were carried out with the same basis set used for the molecule and incorporating the correlation energy, in the case of the ion, by means of the Colle-Salvetti method. The results are −0.4998 and −0.5184 a.u. for H and H^-, respectively. From these results we obtain $\epsilon_0=-0.4998$ a.u. and $U=0.4812$ a.u.

III. RESULTS

We have first attempted to fit the *ab initio* energies of the ground and excited states of neutral hydrogen including only the on-site Coulomb repulsion U. The results are reported in Table I and Fig. 2. Although the fitting is reasonably good, there are several flaws that deserve a comment. The value of U at the equilibrium distance is almost an order of magnitude smaller than its atomic value. The origin of this rather odd result is due to the fact that, for $J=0$, the only way to reproduce the near degeneracy of the first and second excited states given by the *ab initio* calculation at the smallest interatomic distance shown in Fig. 2 is to set $U=0$ [see Eqs. (6) and (7)]. On the other hand, at the largest interatomic distance shown in the figure (4.3 A), U is still far from its atomic value (actually, it is well below 0.4 a.u.). Instead, the energy of the atomic orbital is much closer to its atomic value. In order to understand this behavior we note that at distances beyond which the four states merge into two al-

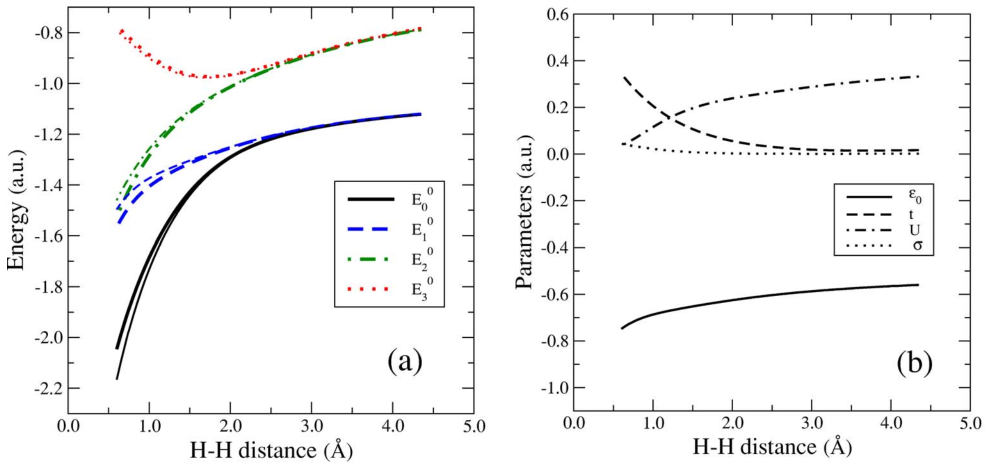

FIG. 2. (Color online) (a) *Ab initio* energies (thick curves) of the ground and excited states of the neutral hydrogen molecule versus the H-H distance. The energies obtained by fitting the parameters of the Hubbard Hamiltonian with $J=0$ [see (b)] to the *ab initio* energies are also shown (thin curves). The ion-ion repulsive energy has been subtracted from the *ab initio* energies. (b) Parameters of the Hubbard Hamiltonian with $J=0$ fitted to give the *ab initio* energies of the ground state and the three excited states of the neutral hydrogen molecule shown in (a).

most degenerate states, the hopping integral t is very small and, thus, the energies of those two states are ϵ_0 and ϵ_0+U, respectively. Therefore, the only way to account for the fact that the difference between those two states keeps growing, even at the largest distances shown in Fig. 2, is an on-site Coulomb repulsion U still varying significantly. If the same set of parameters is used to fit the whole set of states of Table I, the results are very poor. In particular we note that the standard deviation increases by a factor of 4, the differences between *ab initio* and fitted energies being as large as a 30% in the case of the excited state of H_2^+. In addition, at the equilibrium distance U is almost an order of magnitude larger than that obtained from the fitting of the four states of neutral hydrogen. This fully illustrates the deficiencies of a Hamiltonian that just includes the on-site Coulomb repulsion.

Energies and parameters derived from fittings that include the intersite Coulomb repulsion at the equilibrium distance are reported in Table I. Now the error of a fitting of the eight states here considered is only slightly higher than the error of a fitting of just the four states of the neutral molecule with the standard Hubbard model that only includes U. The resulting $U\approx 11.6$ eV is large and close to the atomic value (13.09 eV) although it is only 1.5 times the hopping integral and slightly larger than the intersite Coulomb repulsion $J\approx 8.9$ eV. This small difference between U and J is required to fit also the small energy difference between the first and second excited states of neutral hydrogen. This is most clearly seen in the results for the energies and parameters versus the H-H distance shown in Figs. 3 and 4. At the smallest distance shown in Fig. 3 the first and second excited states of neutral hydrogen are almost degenerate and, as a consequence, U and J are very similar [see Fig. 4(a)]. The energies of the ionized molecule versus the interatomic distance are depicted in Fig. 3(b). Overall, the fittings are rather satisfactory. Finally it is worth noting that the resulting on-site Coulomb repulsion U does not appreciably depend on the interatomic distance being always not far from its atomic value (see Fig. 4)

We have attempted to find the best fit of the numerical results for the intersite electron-electron interaction J and the hopping integral t versus the H-H distance d. The results are

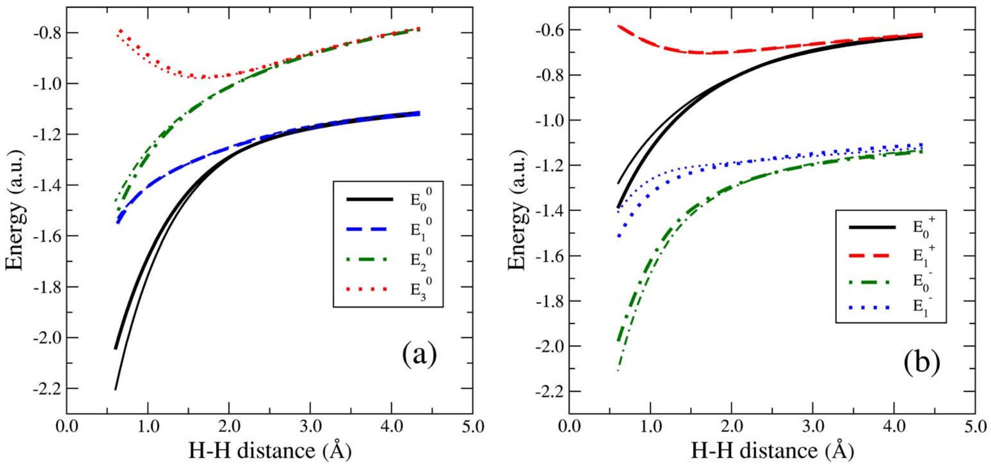

FIG. 3. (Color online) *Ab initio* energies (thick curves) of the ground and excited states of the neutral (a) and singly ionized (b) hydrogen molecules versus the H-H distance. The energies obtained by fitting the parameters of the Hubbard Hamiltonian with finite J (see Fig. 4) to the *ab initio* energies are also shown (thin curves). The ion-ion repulsive energy has been subtracted from the *ab initio* energies.

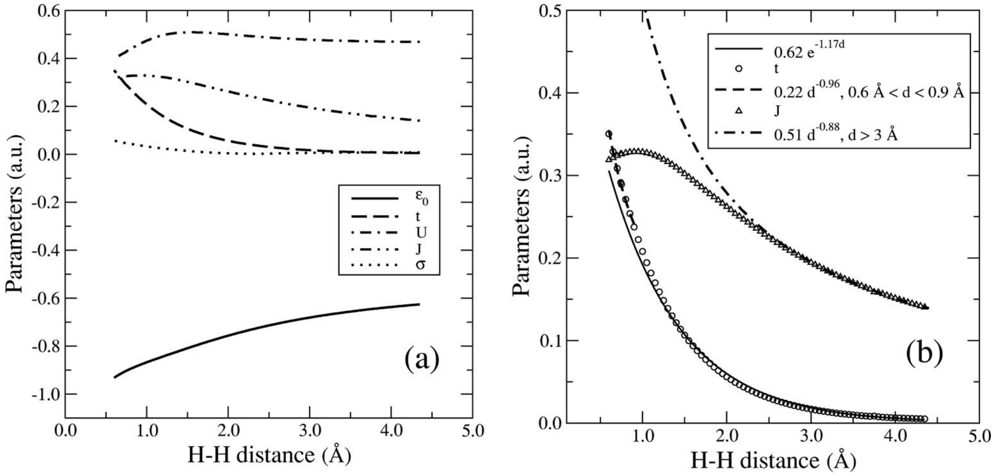

FIG. 4. (a) Parameters of the Hubbard Hamiltonian with finite J fitted to give the *ab initio* energies of the ground and excited states of the neutral and singly ionized hydrogen molecules (see Fig. 3) versus the H-H distance d. (b) Fitting of the numerical results for t and J with the exponential and power functions shown in the inset.

depicted in Fig. 4(b). An exponential satisfactorily fits the results for t over the whole range of H-H distances shown in the figure. This is consistent with the exponential character of the basis set used in the *ab initio* calculations. However, if the fitting is carried out for distances around the equilibrium distance, a fitting close to $1/d$ is also possible. Actually, a $1/d$ scaling law is the one currently used in semiempirical calculations of the band structure of a large variety of solids for the hopping interaction among s-like orbitals.[43] As regards J, we found that at large distances it decreases approximately as $1/d$, as expected (actually, the power 0.88 reported in the figure gets closer to 1 if the fitting is done for increasingly larger H-H distances).

IV. CONCLUDING REMARKS

The results presented in this work indicate that it is possible to fit satisfactorily the energies of the ground states and five excited states of the neutral and singly ionized hydrogen molecule by means of a Hubbard-like model Hamiltonian which includes the intersite electron-electron repulsion. At the equilibrium distance, U is only 24% higher than the intersite Coulomb repulsion and 1.5 times the hopping integral. In addition U shows a weak dependence on the H-H distance, being always close to its atomic value, while J decreases with distance as it should. Our results also point out that a physically meaningful fitting cannot be attained by means of the simplest version of the Hamiltonian that only includes the on-site Coulomb repulsion U. Although these results cannot be extrapolated to cases in which the molecule instead of being free is placed in other chemical environments[14] they may serve as a guideline for the surely required fittings of the particular model parameters.

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