

## NEW POTENTIALS FOR $\text{Si}_2^+$

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The ab initio ground state  $^2\Sigma_g^-$  of  $\text{Si}_2^+$  is studied at the CI level. The ion is found to be bound by 2.48 eV and the state lies 7.0 eV above the ground state of the neutral dimer. Three model potential functions are fitted to the ab initio data and the pertaining parameters are reported.

### 1. Introduction

The chemistry which occurs at the interface between a metal and a silicon cluster is technologically important [1,2]. Despite the practical interest of the problem, little is known about the molecular level mechanism of the reaction. Small clusters offer a new approach to the study of such systems [3] since the stable compound cluster products may represent the early stages of aggregation that form at the interface. However, in the production of silicon clusters by laser vaporization and later analysis by mass spectrometry, there is a dominant abundance of charged photofragments [4]. It is therefore interesting to know more about these charged fragments from a molecular point of view. This is also important so as to understand why in the sputtering of silicon surfaces there is production of positively and negatively charged clusters [5].

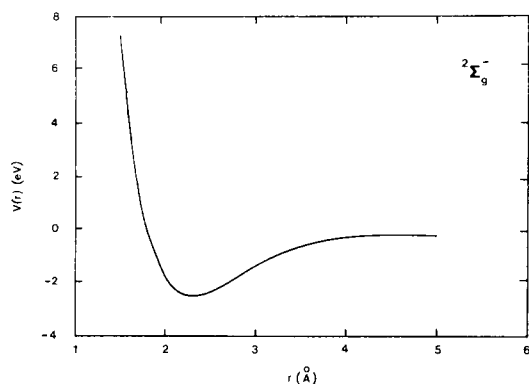
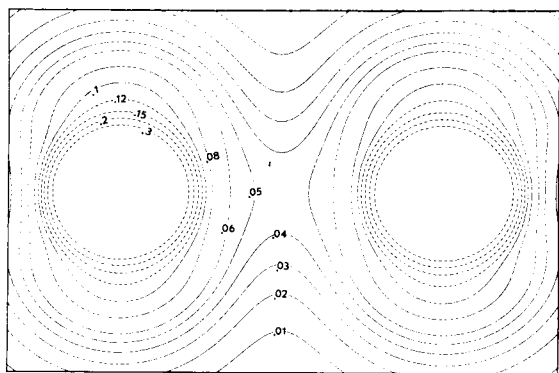
The object of this paper is to present a new interatomic potential for the diatomic cluster  $\text{Si}_2^+$  based on accurate ab initio calculations with the inclusion of electron correlation corrections. We characterize the nature of the ground-state potential curve with special emphasis on the charge distribution along the bond. Though the dimer  $\text{Si}_2$  has been well characterized both spectroscopically [6] and theoretically

[7], considerable uncertainties remain in the nature of the charged silicon clusters, even of  $\text{Si}_2^+$ . Quantum-mechanical results exist for small neutral clusters [7,8], but no calculations exist for charged silicon clusters.

### 2. Molecular orbital considerations and results

The unrestricted Hartree-Fock (UHF) method for doublets was used as the starting point. The standard split-valence plus polarization 6-31G\* basis set [9] was used throughout. In addition, electron correlation effects were included by means of configuration interaction taking into account all the single and double excitations of the valence electrons. The geometry optimization was performed at the CI level. Two levels were found to be close in energy, i.e. the ground state  $^2\Sigma_g^- (1\pi_u^2, 2\sigma_g^1)$  and  $^2\Pi_u (2\sigma_g^2, 1\pi_u^1)$ . For comparison, the ground state of neutral  $\text{Si}_2$  is a  $^3\Sigma_g^- (2\sigma_g^2, 1\pi_u^2)$ , although a  $^1\Sigma_g^+ (1\pi_u^4)$  level lies close by [7]. The calculated electronic structure at the minimum yields: total energy = -577.5933 au,  $D_c = 2.48$  eV,  $r_c = 2.3$  Å. Here  $D_c$  was calculated with respect to the separated atoms  $\text{Si} + \text{Si}^+$ . In fig. 1 we give the  $\text{Si}_2^+$  potential curve in the ground state.  $\text{Si}_2^+$  lies 7.0001 eV above the  $^3\Sigma_g^-$  of the neutral dimer. In fig. 2 we plot the charge density distribution for the ion. Other relevant quantities were obtained at the HF level for the configuration at the minimum of fig. 1. These results are:  $\nu_c = 466.7$  cm<sup>-1</sup>,  $B_c = 6.83$  GHz, charge on each atom = 0.5e, Fermi contact in-

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Fig. 1. The  ${}^2\Sigma_g^-$  ground state of  $\text{Si}_2^+$ .Fig. 2. Charge density level plot of the ground state of  $\text{Si}_2^+$ .

teraction term =  $-0.045$  au, summed gross populations on each atom ( $3s$ ) = 1.9, ( $3p_{\text{AV}}$ ) = 1.0, ( $3p_z$ ) = 0.6. It is interesting to note that the ground state of the ion is formed by removal of a  $p\sigma$  electron (and not a  $\pi_u$ -type electron) and thus the charge is distributed between the two silicon atoms with a considerable stretching of the bond distance (from 2.24 Å in the neutral to 2.3 Å in the ion). The charge density plot shows clearly the covalent character of the bond. This is consistent with what has been reported recently in clustering reactions of  $\text{Si}^+$  with silane [10], in which a bridged ion with a Si-Si<sup>+</sup> bond of 2.33 Å was found to be very stable.

### 3. Model potential functions

Historically, the atom-atom potential models were first obtained from fitting various experimental re-

sults of bulk materials. Recently, however, it has been demonstrated that the potentials that simulate well the interactions in condensed phases very seldom reproduce the properties of clusters [11]. More attempts are therefore necessary to simulate the results of rigorous quantum-mechanical calculations [12]. The principal objective of such studies is: (1) to clarify the nature of the atom-atom potentials, and (2) to develop easily computable model potentials that can be used in repeated calculations of the interaction energy of larger systems.

To the curve in fig. 1 we have fitted the parameters of three model potentials that can be used in future simulation studies of larger clusters and interfaces. Only recently more attention has been given to produce good potentials for silicon [13]. These new potentials emphasize, however, on the directionality of the bonding in silicon by proposing empirical three-body potentials. Apparently very few potentials have been produced for charged dimers [14] in general, and in particular none for the group IVA elements. We tested three functions and will refer to these potentials as RB1, RB2 and RB3. The fit was done using the Levenberg-Marquardt algorithm and the sum of least squares  $S$  gives a measure of the quality of the fit. Units will be given in atomic units (hartree for energy). The model potentials are:

(1) RB1 is the Morse potential

$$V(r) = D_e \{1 - \exp[-\beta(r - r_e)]\}^2 - D_e$$

with parameters  $D_e = 0.09133$ ,  $\beta = 0.78185$ ,  $r_e = 4.3316$ . Alternatively this potential can be written as

$$V(r) = A \exp(-\lambda_1 r) - B \exp(-\lambda_2 r), \quad (1)$$

where  $A = 79.842$ ,  $B = 5.4007$ ,  $\lambda_1 = \beta = 2\lambda_2$  and  $S = 0.002$ .

(2) RB2 with four parameters:

$$V(r) = A(B/r^4 - 1) \exp[\gamma/(r-a)], \quad \text{if } r < a, \\ = 0, \quad \text{otherwise,} \quad (2)$$

where  $A = 2.6121$ ,  $B = 132.6443$ ,  $\gamma = 17.8684$ ,  $a = 10.5$ , and  $S = 0.0095$ .

(3) RB3 with four parameters:

$$V(r) = A \exp(-\alpha r) - C/r^n, \quad (3)$$

where  $A=157.27$ ,  $\alpha=1.6778$ ,  $C=70.105$ ,  $p=4$  and  $S=0.01$ .

$\text{Si}_2^+$  behaves as a good bound diatomic; the bond is nicely reproduced by the Morse potential (RB1). This pairwise potential is the function used by Tersoff [13] for neutral silicon to account for the spherically symmetric part of his potential. However, the possibility to represent the bond by other functions is feasible as shown by RB2 and RB3. The second function, RB2, has the same functional form used by Stillinger and Weber [13], to represent the pair potential for neutral Si. The parameters for the ion are, however, considerably different – the repulsion is larger in the bond region, the ion is more bonded and the cutoff distance is increased by 20%. The third of these functions is a refinement of what we used in the past [11] to give a rough representation of the dispersion energy of a localized charge in a cluster. In this calculation the dispersion energy was obtained considering the atomic polarizability of silicon. The new parameters for the ion show that the interaction is less attractive in the bonding region but becomes more important at long distances. The three functions have in common a soft repulsive core and are of relatively short range (of the order of 10.5 au). These same features were observed for the neutral dimer as well.

Dimers from the group IVA,  $\text{Si}_2$ ,  $\text{Ge}_2$ ,  $\text{Sn}_2$  and  $\text{Pb}_2$ , have all the same ground state  $^3\Sigma_g^-$  with an excitation energy of 1.0–1.5 eV to the  $^1\Sigma_g^+$  [15]. On the contrary the ground state of  $\text{C}_2$  is a  $^1\Sigma_g^+$  with excitation energies of 0.09 and 0.8 eV to the  $^3\Pi_u$  and  $^3\Sigma_g^-$  states, respectively. In fact, the absence of core p states and the compact 2p valence functions apply to all first-row atoms, not just beryllium [12]. These atoms show qualitative differences in their binding properties from atoms in the remainder of the periodic table. The ease of  $\sigma_g \rightarrow \pi_u$  transfer and strong bonds is therefore a peculiarity to the C–C bond. These same trends rest to be studied in the corresponding ions.

#### 4. Conclusion

Accurate theoretical calculations have been performed to study the ground state of the silicon dimer ion. This state is a  $^3\Sigma_g^-$  in which the charge is equally

distributed on each atom. In addition three model potentials have been proposed to represent this covalent ion. All of them show that the repulsive core is stronger than in the neutral dimer and that the range of the interaction is considerably longer. Other dimeric ions of the IVA elements should be studied to draw any general conclusion along the series.

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