

Potential Functions of Al₂ by the Relativistic Fock-Space Coupled Cluster Method

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Abstract: Potential functions of the ground and low excited states of Al₂ are calculated by the relativistic Fock-space coupled cluster method in the framework of the projected Dirac-Coulomb Hamiltonian. A moderate-size basis [16s11p3d3f/6s6p3d2f] is used. ³Π_u is confirmed as the ground state of the system. Its spin orbit splittings are reproduced well, with the Λ = 1, 2 states lying 32.5 and 66.1 cm⁻¹, respectively, above the Λ = 0 minimum (experimental values are 30.4 and 63.4 cm⁻¹). The bond is somewhat too weak, with D_e 0.14 eV below experiment, R_e too high by 0.08 Å, and ω_e 21 cm⁻¹ too low. It is speculated that the better agreement obtained in earlier calculations may be due to neglect of basis set superposition errors. The description of bonding in the molecule may be improved by the use of a better basis and the inclusion of more correlation by the intermediate Hamiltonian coupled cluster method, which makes it possible to handle larger *P* spaces and extend the potential functions to the whole range of internuclear separations.

Keywords: Aluminum dimer; Relativistic coupled cluster; Intermediate Hamiltonian coupled cluster.

1 Introduction

The aluminum dimer, a light molecule with only two valence electrons, exhibits nevertheless interesting features in its bonding. The $3p$ valence electrons can go into either $p\sigma_g$ or $p\pi_u$ bonding orbitals, yielding a number of close-lying potential curves. The nature of the ground state was not clear for many years (references to early work may be found in [1]); more recently, both theoretical [2,3] and experimental [1,4] studies identified the ground state as $\sigma_g\pi_u X^3\Pi_u$, followed closely by $\pi_u^2 A^3\Sigma_g^-$. The adiabatic energy separation T_e of the two states has not been determined experimentally; theoretical predictions [2,3] are about 200 cm^{-1} .

An interesting feature of the Al_2 ground state is its spin-orbit splitting [4]. The lowest state is $^3\Pi_{0u}$, with $^3\Pi_{1u}$ and $^3\Pi_{2u}$ 30.4 and 63.4 cm^{-1} higher, respectively. The $\Omega = 0$ state itself is split into $^3\Pi_{0-u}$ and $^3\Pi_{0+u}$, separated by 0.087 cm^{-1} . These splittings were not accounted for in previous calculations, which were nonrelativistic and did not include spin-orbit coupling.

The purpose of the present work is to apply the relativistic Fock-space coupled cluster method to the low states of Al_2 . This method has proved highly accurate for energy levels of heavy atoms, reproducing transition energies (ionization potentials, excitation energies, electron affinities) within a few hundredths of an eV in most cases and providing reliable predictions for super-heavy elements, where ground and excited state configurations are often different from those of lighter homologs (for a recent review see [5]). The reduced symmetry of molecules increases dramatically the computational resources required and limits the size of the basis which can be used. This work should be regarded as preliminary, with a modest-size basis, and is expected to pave the way to more complete applications in the future.

2 Methodology

2.1 The relativistic Hamiltonian

The relativistic many-electron Hamiltonian cannot be written in closed form; it may be derived perturbatively from quantum electrodynamics [6]. The simplest form is the Dirac-Coulomb (DC) Hamiltonian, where the nonrelativistic one-electron terms in the Schrödinger equation are replaced by the one-electron Dirac operator h_D ,

$$H_{\text{DC}} = \sum_i h_D(i) + \sum_{i<j} 1/r_{ij}, \quad (1)$$

with

$$h_D = c\boldsymbol{\alpha} \cdot \mathbf{p} + \beta c^2 + V_{\text{nuc}}. \quad (2)$$

$\boldsymbol{\alpha}$ and β are the four-dimensional Dirac matrices, and V_{nuc} is the nuclear attraction operator, with the nucleus modeled as a point or finite-size charge. Only the one-electron terms in the DC

Hamiltonian include relativistic effects, and the two-electron repulsion remains in the nonrelativistic form.

The DC Hamiltonian may lead to the admixture of negative-energy eigenstates of the Dirac Hamiltonian in an erroneous way [7, 8]. The no-virtual-pair approximation [9, 10] is invoked to correct this problem: the negative-energy states are eliminated by the projection operator Λ^+ , leading to the projected Hamiltonians

$$H_{\text{DC}}^+ = \Lambda^+ H_{\text{DC}} \Lambda^+ . \quad (3)$$

H_{DC}^+ provides the framework for the calculations reported here.

2.2 The Fock space coupled cluster method

The Dirac-Coulomb Hamiltonian H_{DC}^+ may be rewritten in second-quantized form [9, 11] in terms of normal-ordered products of spinor creation and annihilation operators $\{r^\dagger s\}$ and $\{r^\dagger s^\dagger ut\}$,

$$H = H_{\text{DC}}^+ - \langle 0 | H_{\text{DC}}^+ | 0 \rangle = \sum_{rs} f_{rs} \{r^\dagger s\} + \frac{1}{4} \sum_{rstu} \langle rs || tu \rangle \{r^\dagger s^\dagger ut\}, \quad (4)$$

where

$$\langle rs || tu \rangle = \langle rs | tu \rangle - \langle rs | ut \rangle$$

and

$$\langle rs | tu \rangle = \int d\mathbf{x}_1 d\mathbf{x}_2 \Psi_r^*(\mathbf{x}_1) \Psi_s^*(\mathbf{x}_2) r_{12}^{-1} \Psi_t(\mathbf{x}_1) \Psi_u(\mathbf{x}_2).$$

Here f_{rs} and $\langle rs || tu \rangle$ are, respectively, elements of one-electron Dirac-Fock and antisymmetrized two-electron Coulomb interaction matrices over Dirac four-component spinors. The effect of the projection operators Λ^+ is now taken over by normal ordering, denoted by the curly braces in (4), which requires annihilation operators to be moved to the right of creation operators as if all anticommutation relations vanish. The Fermi level is set at the top of the highest occupied positive-energy state, and the negative-energy states are ignored.

By adopting the no-pair approximation, a natural and straightforward extension of the nonrelativistic open-shell CC theory emerges. The multireference valence-universal Fock-space coupled-cluster approach is employed, which defines and calculates an effective Hamiltonian in a low-dimensional model (or P) space, with eigenvalues approximating some desirable eigenvalues of the physical Hamiltonian. The effective Hamiltonian has the form [12]

$$H_{\text{eff}} = PH\Omega P \quad (5)$$

where Ω is the normal-ordered wave operator,

$$\Omega = \{\exp(S)\}. \quad (6)$$

The Fock-space approach starts from a reference state (closed-shell in our applications, but other single-determinant functions may also be used), correlates it, then adds and/or removes electrons one at a time, recorrelating the whole system at each stage. The sector (m, n) of the Fock space includes all states obtained from the reference determinant by removing m electrons from designated occupied orbitals, called valence holes, and adding n electrons in designated virtual orbitals, called valence particles. The practical limit is $m + n \leq 2$, although higher sectors have also been tried [13]. The excitation operator is partitioned into sector operators

$$S = \sum_{m \geq 0} \sum_{n \geq 0} S^{(m,n)}. \quad (7)$$

This partitioning allows for partial decoupling of the open-shell CC equations. The equations for the (m, n) sector involve only S elements from sectors (k, l) with $k \leq m$ and $l \leq n$, so that the very large system of coupled nonlinear equations is separated into smaller subsystems, which are solved consecutively: first, the equations for $S^{(0,0)}$ are iterated to convergence; the $S^{(1,0)}$ (or $S^{(0,1)}$) equations are then solved using the known $S^{(0,0)}$, and so on. This separation, which does not involve any approximation, reduces the computational effort significantly. The effective Hamiltonian (5) is also partitioned by sectors. An important advantage of the method is the simultaneous calculation of a large number of states. Reviews of the Fock-space method may be found in Refs. [14, 15].

Each sector excitation operator is, in the usual way, a sum of virtual excitations of one, two, ..., electrons,

$$S^{(m,n)} = \sum_l S_l^{(m,n)}, \quad (8)$$

with l going, in principle, to the total number of electrons. In practice, l has to be truncated. The level of truncation reflects the quality of the approximation, i.e., the extent to which the complementary Q space is taken into account in the evaluation of the effective Hamiltonian. In the applications described below the series (8) is truncated at $l=2$. The resulting CCSD (coupled cluster with single and double excitations) scheme involves the fully self-consistent, iterative calculation of all one- and two-body virtual excitation amplitudes and sums all diagrams with these excitations to infinite order. As negative-energy states are excluded from the Q space, the diagrammatic summations in the CC equations are carried out only within the subspace of the positive-energy branch of the DF spectrum.

2.3 The intermediate Hamiltonian coupled cluster method

The accuracy and convergence of the Fock-space coupled cluster method discussed above depends on an appropriate partitioning of the function space into P and Q subspaces. Ideally, the P

space should include all functions which are important to the states considered, since the effective Hamiltonian is diagonalized in P , whereas Q -space contributions are included approximately. On the other hand, convergence of the coupled cluster iterations is enhanced by maximal separation and minimal interaction between P and Q . These two requirements are not always easy to reconcile. Relatively high P functions have often strong interaction with or are energetically close to Q states, making convergence slow or impossible. The offending functions are usually included in P because of their significant contribution to the lower P states, and we may not be particularly interested in the correlated states generated from them by the wave operator; however, the FSCC is an all-or-nothing method, and lack of convergence means that no states at all are obtained. The intermediate Hamiltonian coupled cluster method developed recently [16] addresses this problem, making possible larger and more flexible P spaces, thereby extending the scope of the coupled cluster method and increasing its precision.

The intermediate Hamiltonian method has been proposed by Malrieu [17] in the framework of degenerate perturbation theory. The P space is partitioned into the main P_m and the intermediate P_i , with the corresponding operators satisfying

$$P_m + P_i = P, \quad P + Q = 1. \quad (9)$$

Two sets of wave-like operators are defined and expanded in coupled-cluster normal-ordered exponential ansätze. $\Omega = 1 + \chi$ is a standard wave operator in P_m ,

$$\Omega P_m |\Psi_m\rangle = \{\exp S\} P_m |\Psi_m\rangle = |\Psi_m\rangle, \quad (10)$$

where $|\Psi_m\rangle$ denotes an eigenstate of the Hamiltonian H with the largest components in P_m , and $R = 1 + \Delta$ is an operator in P , satisfying

$$R P |\Psi_m\rangle = \{\exp T\} P |\Psi_m\rangle = |\Psi_m\rangle. \quad (11)$$

It should be noted that the last equation, and therefore all equations derived from it, applies when operating on $|\Psi_m\rangle$ but not necessarily on $|\Psi_i\rangle$. This feature distinguishes R from a bona fide wave operator. The cluster equation for S in the (n) sector of the Fock space is [16]

$$Q[S^{(n)}, H_0]P_m = Q(\overline{VQ_i\Omega} - \overline{\chi P_m VQ_i\Omega})^{(n)}P_m, \quad (12)$$

where $Q_i = 1 - P_i = Q + P_m$. No $P_i S P_m$ elements appear in the equation, so that P_i acts as a buffer between P_m and Q , facilitating convergence and avoiding intruder states. Eq. (12) is valid provided $Q S P_m \simeq Q T P_m$, which is rather easy to achieve and is checked in the calculation. After (12) is solved for $Q S P_m$, the equation for $Q T P$ is solved,

$$(E - H_0) Q T^{(n)} P = \quad (13)$$

$$Q \left(S(E - H_0) P_m + (\overline{V R}) - (\overline{\chi P_m V R}) \right)^{(n)} P.$$

E is an arbitrary constant, chosen to facilitate convergence. Tests have shown that E may be changed within broad bounds (hundreds of hartrees) with minute effect (a few wave numbers) on calculated transition energies. The final step is the construction of the intermediate Hamiltonian

$$H_I = P H R P, \quad (14)$$

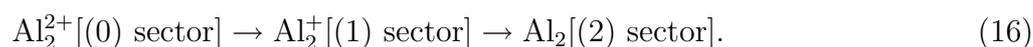
which gives upon diagonalization the correlated energies of $|\Psi_m\rangle$,

$$H_I P |\Psi_m\rangle = E_m P |\Psi_m\rangle. \quad (15)$$

The dimension of the H_I matrix is that of P ; however, only the eigenvalues corresponding to $|\Psi_m\rangle$ are required to satisfy (15). The other eigenvalues, which correspond to states $|\Psi_i\rangle$ with the largest components in P_i , may include larger errors.

3 Calculations

The MOLFDIR [18] program package was used in the Dirac-Fock stage of the calculations, generating the orbitals and integrals needed in the coupled cluster part. The augmented correlation consistent pVTZ basis [19] was recontracted by Partridge *et al.* [20]. It consists of 16s11p3d3f Gaussian-type spinors contracted to 6s6p3d2f. It is a moderate-size basis, and is expected to give good but not definitive results. As indication to the quality of the basis, the ionization potential of atomic Al given by it at the Fock-space CCSD level is 5.88 eV, compared with the experimental [21] 5.98 eV, and the ${}^2P_{3/2} - {}^2P_{1/2}$ splitting is 119 cm^{-1} , close to the experimental [22] 112 cm^{-1} . The closed-shell Al_2^{2+} ion was used as reference, and the Al_2 states were obtained by the Fock-space scheme



All electrons were correlated, except the inner-shell 1s. Double-group symmetry was used, and the valence orbitals were $6'e_{1g}$, $6''e_{1g}$, $6'e_{1u}$, $6''e_{1u}$, $2'e_{2u}$, and $2''e_{2u}$, all the bonding molecular orbitals resulting from the Al 3p atomic orbitals. Virtual orbitals with energies above 100 a.u. were discarded; all other excitations were included in the coupled cluster expansion. Results were corrected for basis set superposition errors (BSSE) by the counterpoise method [23].

4 Results and Discussion

Calculated energies of the Al_2 low-lying triplet and singlet states are collected in tables 1 and 2, respectively. Potential functions are shown in fig. 1. Spectroscopic constants for the different states are listed in table 3. To our knowledge, this is the first calculation of the fine-structure

Table 1: Calculated energies of Al₂ triplets. All quantities in atomic units. 484 a.u. should be subtracted from listed values to obtain the total energies.

R	³ Π _{0+u}	³ Π _{0-u}	³ Π _{1u}	³ Π _{2u}	³ Σ _g ⁻
4.2	-0.9316700	-0.9316700	-0.93149	-0.93131	-0.95592
4.8	-0.9475860	-0.9475860	-0.94741	-0.94724	-0.96414
4.6	-0.9579970	-0.9579970	-0.95783	-0.95766	-0.96791
4.8	-0.9642450	-0.9642450	-0.96418	-0.96401	-0.96856
5.0	-0.9676862	-0.9676851	-0.96753	-0.96737	-0.96711
5.2	-0.9688693	-0.9688680	-0.96872	-0.96856	-0.96429
5.4	-0.9684924	-0.9684909	-0.96835	-0.96819	-0.96064
5.6	-0.9670160	-0.9670150	-0.96687	-0.96672	-0.95650
5.8	-0.9647870	-0.9647850	-0.96464	-0.96450	-0.95219
6.2	-0.9590180	-0.9590150	-0.95888	-0.95873	-0.94361
6.4	-0.9558050	-0.9558020	-0.95566	-0.95552	-0.93956

Table 2: Calculated energies of Al₂ singlets. All quantities in atomic units. 484 a.u. should be subtracted from listed values to obtain the total energies.

R	¹ Π _u	(1) ¹ Σ _g ⁺	(2) ¹ Σ _g ⁺	¹ Δ _g
4.2	-0.91804	-0.92544	-0.87523	-0.93929
4.4	-0.93415	-0.93743	-0.89657	-0.94851
4.6	-0.94472	-0.94544	-0.91091	-0.95324
4.8	-0.95120	-0.95084	-0.91982	-0.95482
5.0	-0.95466	-0.95449	-0.92466	-0.95426
5.2	-0.95595	-0.95683	-0.92664	-0.95230
5.4	-0.95567	-0.95805	-0.92673	-0.94946
5.6	-0.95431	-0.95838	-0.92568	-0.94612
5.8	-0.95220	-0.95790	-0.92395	-0.94256
6.2	-0.94678	-0.95523	-0.91966	-0.93539
6.4	-0.94380	-0.95328	-0.91743	-0.93199

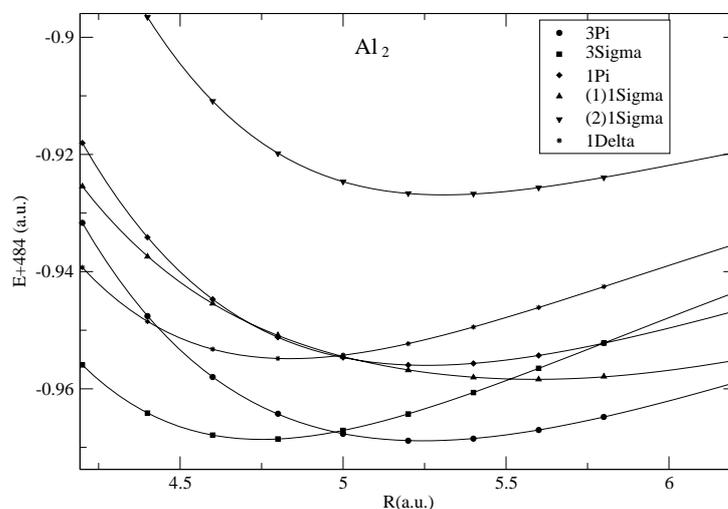


Figure 1: Al_2 potential functions. Splitting of the $^3\Pi_u$ state not shown.

splittings of the ground $^3\Pi_u$ state. The splittings between the $\Omega = 0, 1, 2$ states are reproduced well, with calculated values of 32.5 and 66.1 cm^{-1} compared with the experimental [4] 30.4 and 63.4. The Λ doubling splits the $^3\Pi_{0u}$ level; the calculated splitting (0.3 cm^{-1}) is larger than the experimental 0.09 cm^{-1} . This is, however, a very small effect. The deficiencies in the basis lead to a bond which is somewhat too weak: D_e is calculated at 1.22 eV, vs. the experimental [4] 1.36 ± 0.06 ; R_e is 2.78 Å (experimental 2.70); and ω_e is 265 cm^{-1} (experimental 286). It should be noted that results uncorrected for BSSE give, as expected, a stronger bond ($D_e=1.37$ eV, $R_e=2.74$ Å, $\omega_e=281$ cm^{-1}). This is due to cancellation of errors. Langhoff and Bauschlicher [3] do not mention the BSSE correction; their values, which are close to our uncorrected numbers, may indicate that the correction was not applied. The $\text{A}^3\Sigma_g^-$ spectroscopic constants show similar behavior, with the calculated R_e 2.52 Å compared with the experimental [4] 2.47 Å, $\omega_e = 335$ cm^{-1} (expt. 350 cm^{-1}), and $\omega_e x_e = 2.0$ cm^{-1} (expt. 2.0 cm^{-1}). Values uncorrected for BSSE are again closer to experiment and to the Langhoff and Bauschlicher numbers.

While the results shown here are satisfactory, in particular the splittings of the ground state, they are far from definitive. These calculations should be improved in two directions: a more complete basis set is needed, and the treatment of correlation should be better. The latter goal might be achieved by the use of the intermediate Hamiltonian coupled cluster method [16] discussed above. This new method will also remove the limitation on the range of internuclear distances calculated. The current application uses only bonding orbitals constructed from atomic $3p$ as va-

Table 3: Spectroscopic constants of Al₂ states.

State	r_e (Å)	D_e (eV)	ω_e	$\omega_e x_e$	T_e (cm ⁻¹)
³ Π _{0-u}	2.78	1.21	265	0.91	0
³ Π _{0+u}	2.78	1.22	265	0.90	0.3
³ Π _{1u}	2.78	1.21	266	1.4	32.7
³ Π _{2u}	2.78	1.22	266	1.4	66.3
³ Σ _g ⁻	2.52	1.22	335	2.0	70.7
(1) ¹ Σ _g ⁺	2.95	0.94	200	1.6	2310
¹ Π _u	2.79	0.88	262	1.6	2830
¹ Δ _g	2.57	0.85	310	2.1	3080
(2) ¹ Σ _g ⁺	2.81	0.10	264	2.9	9240

lence orbitals. Bonding and antibonding orbitals become closer in energy as R increases, leading to the appearance of intruder states and causing convergence difficulties in the Fock-space method. The intermediate Hamiltonian method can handle larger and more flexible P spaces, comprising both bonding and antibonding $3p$ orbitals. Preliminary calculations show that the intruder state problem is indeed solved, and the potential functions may be calculated over the whole range of internuclear separations. These calculations are under way, and results will be reported elsewhere.

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