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Application of open-shell coupled cluster theory to the ground state of GaAs

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Summary. Theoretical calculations at the coupled cluster level of theory including all single, double and perturbative triple excitations, CCSD(T), are carried out for the $^3\Sigma^-$ ground state of GaAs. Employing a $(7s5p3d1f)$ basis set, the theoretical predictions for r_e (2.560 Å), ω_e (217 cm^{-1}), D_e (1.84 eV), and IP (7.80 eV), are in good agreement with recent experimental results. The importance of including f-type polarization functions in the basis set and the effect of correlating $3d$ electrons are discussed in detail.

Key words: GaAs ground state – CCSD(T) – f-type polarization functions

1. Introduction

GaAs semiconductors are of technological importance because they are useful in constructing fast devices. Smalley and co-workers [1] have generated supersonic beams of semiconductor clusters of formula Ga_xAs_y by laser vaporization of pure GaAs. Recently, Lemire, Bishea, Heidecke and Morse [2] (LBHM) obtained an optical spectrum for diatomic GaAs by resonant two-photon ionization spectroscopy. The ground state was identified as $X\,^3\Sigma^-$ and characterized by $\omega_e = 215$ cm^{-1} and $r_0 = 2.53 \pm 0.02$ Å. The ionization potential of GaAs was also experimentally bracketed as IP(GaAs) $= 7.17 \pm 0.75$ eV and the dissociation energy estimated as $D_0 = 2.06 \pm 0.05$ eV.

Two theoretical *ab initio* studies have been reported for GaAs in the past. Balasubramanian [3] carried out calculations on the low-lying states of GaAs and GaAs$^+$ employing complete active space (CASSCF) first order configuration interaction wavefunctions in conjunction with effective core potentials for the inner shells. This author found 6 bound states in GaAs and the ground state was predicted to be $^3\Sigma^-$. This result has been recently confirmed by LBHM [2]. However, Balasubramanian's predictions [3] for the equilibrium bond-length (2.645 Å), the harmonic vibrational frequency (187 cm^{-1}), the ionization potential (5.91 eV), and the dissociation energy (1.17 eV), are not in good agreement with the experimental results [2].

In another recent paper, Meier, Peyerimhoff, Bruna and Green [4] (MPBG) have also studied the low-lying electronic states of GaAs and GaAs$^+$ by multireference configuration interaction theory including double excitations (MRD-CI). This method is based on configuration selection and energy extrapolation. These authors studied the importance of correlating the inner 3*d* electrons on different properties. Employing an 8*s*6*p*3*d* basis set, their calculated equilibrium bond-length and vibrational frequency for GaAs at the MRD-CI level of theory was 2.60 Å and 202 cm^{-1}, respectively. When 3*d*-electron correlation effects were taken into account, the calculated values were 2.58 Å and 203 cm^{-1}, respectively. They also obtained 6.94 eV for the vertical IP of GaAs and $D_e = 1.60$ eV. MPBG's results are in better qualitative agreement with the experimental results [2].

In this work, a different theoretical approach is pursued. The starting point is a single-reference open-shell restricted Hartree–Fock (RHF) determinant and both dynamical and non-dynamical correlation effects are accounted for by means of a coupled-cluster (CC) expansion [5–9]. Two different levels of CC theory were employed in this work, namely, CC theory including all single and double excitations (CCSD) [10], and CCSD plus a perturbative correction due to triple excitations [CCSD(T)] [11]. The main difference between the present scheme and the methods previously used for this problem is that no multi-reference wavefunctions are employed in this work. Additionally, the effect of including *f*-functions in the basis set has been herein analyzed.

In the next section computational details are summarized. The theoretical predictions for r_e, ω_e, IP and D_e of $X\,^3\Sigma^-$ are presented and compared with other *ab initio* studies in the following section.

2. Computational details

Two basis sets were used in this work. For both atoms (Ga and As), Dunning's 14*s*11*p*5*d* primitive set [12] was contracted to 7*s*5*p*2*d* employing the scheme 6112211-61211-41. In a previous extensive study of As_2 [13], it was shown that such contraction scheme gives satisfactory agreement with uncontracted SCF results for this molecule. A *d*-polarization function was added to this basis set with exponents $\alpha_d(\mathrm{Ga}) = 0.16$ and $\alpha_d(\mathrm{As}) = 0.25$. The resulting basis sets is denoted (7*s*5*p*3*d*). The second basis set employed in this work, (7*s*5*p*3*d*1*f*), is obtained from the (7*s*5*p*3*d*) basis by adding one set of *f*-functions with exponents $\alpha_f(\mathrm{Ga}) = 0.16$ and $\alpha_f(\mathrm{As}) = 0.25$. Only the pure spherical components of the *d*- and *f*-type functions have been included in the basis sets employed in this study.

All-electron restricted Hartree–Fock (RHF) calculations were carried out on the $^3\Sigma^-$ ground state of GaAs with these basis sets. Correlation effects were based upon open-shell coupled cluster theory including single and double excitations (CCSD) [10, 14], and CCSD plus perturbative triple corrections [CCSD(T)] [11, 15–17]. The CCSD(T) method adds one fifth-order term in perturbation theory to the CCSD + T(CCSD) method [18, 19]. The Ga and As 1*s*, 2*s*, 2*p*, 3*s* and 3*p* orbitals were kept doubly occupied in all correlated calculations whereas the 3*d* orbitals were selectively kept active or inactive (doubly occupied) in all configurations. The active shells are indicated in parentheses following the specific theoretical method, i.e. CCSD (4) or CCSD(T) (3*d*, 4). The number of correlated electrons is 8 (4*s*, 4*p*) and 28 (3*d*, 4*s*, 4*p*). A previous study [13] on As_2 has shown that correlation effects from the 3*s* and 3*p* electrons play a minor role in this molecule when compared with the 3*d* electron correlation effects.

The open-shell coupled cluster calculations were carried out using a recently developed program [20] based on single-reference open-shell RHF functions that does not include any spin contamination in the correlation energy. This method is similar to the projected RHF-CC method of Rittby and Bartlett [21–26].

Equilibrium bond-lengths and harmonic vibrational frequencies were obtained by finite differences of energies. The error bars in the theoretical predictions due to numerical differentiation were kept smaller than 10^{-3} Å and 1 cm^{-1}, respectively. Calculations at Rice University were performed on a MIPS M-2000 computer.

3. Results and discussion

Results obtained in this work are presented in Table 1.

With both basis sets, the effect of triple excitations on the equilibrium bond-length is fairly small. The predicted r_e at the CCSD(T) level of theory is ~0.005 Å longer than the value obtained with the CCSD method, both including and excluding $3d$-electron correlation effects. At a given level of theory (CCSD or CCSD(T)), the inclusion of $3d$-electron correlation effects is more important: equilibrium bond-lengths are shortened by 0.02–0.03 Å in all cases. The inclusion of f-type polarization functions in the basis set results in an additional shortening of r_e by 0.014–0.025 Å depending on the specific level of theory. The predicted r_e at the $(7s5p3d1f)$/CCSD(T) $(3d, 4)$ level of theory is 2.560 Å. This value is 0.03 Å longer than the experimental r_0.

Harmonic vibrational frequencies predicted in this study for the ground state of GaAs are all within the 206–219 cm^{-1} range. In general, longer bond-lengths

Table 1. Total energy,[a] equilibrium bond-length, vibrational frequency, dissociation energy and vertical ionization potential of $X\,{}^3\Sigma^-$ GaAs as predicted by the coupled cluster method

Basis and method	E (h)	r_e (Å)	ω_e (cm^{-1})	D_e (eV)	IP (eV)
$(7s5p3d)$					
SCF	−0.091111	2.580	217	0.84	6.40
CCSD (4)	−0.232030	2.603	208	1.44	6.71
CCSD(T) (4)	−0.236325	2.608	206	1.51	6.70
CCSD $(3d, 4)$	−0.497519	2.580	211	1.47	6.63
CCSD(T) $(3d, 4)$	−0.510311	2.585	208	1.55	6.62
$(7s5p3d1f)$					
SCF	−0.092750	2.566	219	0.89	6.89
CCSD (4)	−0.249695	2.586	214	1.68	7.51
CCSD(T) (4)	−0.255794	2.591	212	1.75	7.58
CCSD $(3d, 4)$	−0.520285	2.556	219	1.75	7.71
CCSD(T) $(3d, 4)$	−0.535393	2.560	217	1.84	7.80
CASSCF-FOCI[b]		2.645	187	1.17	5.91
MRD-CI (4)[c]	−0.4121	2.60	202	1.40	6.94
MRD-CI $(3d, 4)$[c]	−0.6605	2.58	203	1.60	
Experimental[d]		2.53	215	2.06	7.17

[a] Energies are reported as $E + 4157$ h

[b] Balasubramanian (Ref. [3])

[c] Meier, Peyerimhoff, Bruna, and Grein (Ref. [4])

[d] Lemire, Bishea, Heidecke, and Morse (Ref. [2])

correlate with smaller frequencies. At the highest level of theory employed in this work, (7*s*5*p*3*d*1*f*)/CCSD(T) (3*d*, 4), the harmonic vibrational frequency of $^3\Sigma^-$ GaAs (217 cm^{-1}) is only 2 cm^{-1} apart from the experimental result. It is interesting to note that with both basis sets, the SCF predictions for r_e and ω_e are numerically close to the CC (3*d*, 4) predictions. In particular, with the (7*s*5*p*3*d*1*f*) basis set, the SCF results (2.566 Å and 219 cm^{-1}) are very close to the CCSD(T) (3*d*, 4) predictions of 2.560 Å and 217 cm^{-1}, respectively. This fortuitous cancellation of errors at the SCF level of theory is not valid for the other two properties (D_e and IP) studied in this work.

The dissociation energy of $^3\Sigma^-$ GaAs is underestimated by all methods and bases employed in this work. It it interesting to compare results obtained by including and excluding *f*-functions at a given level of theory. At the SCF level, the effect of including *f*-functions on D_e is only 0.05 eV. However, when electron correlation effects are included, the effect of *f*-functions varies between 0.24 (CCSD (4)) to 0.29 eV (CCSD(T) (3*d*, 4)). It is evident that there is a large coupling between the one- and *n*-particle basis for the dissociation energy of this molecule. Results presented in Table 1 indicate that while the CCSD(T) method is capable of including the most important correlation effects in the wavefunction, the remaining basis set error may be mainly responsible for the 0.22 eV difference between the (7*s*5*p*3*d*1*f*)/CCSD(T) (3*d*, 4) prediction of 1.84 eV and the experimental 2.06 eV result. The basis set superposition error (bsse) for the dissociation energy was estimated in this work using the counterpoise method [27] in the presence of the full ghost basis at the GaAs equilibrium geometry (i.e. As and Ga atomic energies were evaluated in the presence of the full ghost Ga and As bases, respectively). With the larger (7*s*5*p*3*d*1*f*) basis set, the calculated D_e after bsse corrections are 0.81, 1.57, 1.65, 1.58 and 1.67 eV, at the SCF, CCSD (4), CCSD(T) (4), CCSD (3*d*, 4), and CCSD(T) (3*d*, 4) levels of theory, respectively. Taking this correction into account, the difference between the best calculated and experimental D_e value is 0.39 eV.

The vertical ionization potential is obtained in this work as the energy difference between the $X\ ^3\Sigma^-$ of GaAs and the $^4\Sigma^+$ ground state of GaAs$^+$. Results reported in Table 1 show that this property is fairly insensitive to the correlation level and to the number of correlated electrons. In analogy with D_e, the basis set effect seems to be predominant. The (7*s*5*p*3*d*1*f*)/CCSD(T) (3*d*, 4) value of 7.80 eV predicted in this work is in the upper portion of the experimental bracket (6.42–7.92 eV).

In Table 1 the CC results are also compared with other recent *ab initio* predictions. The 0.02 Å bond-length shortening obtained by MPBG when correlating 3*d*-electrons is in good agreement with the present results. Their calculated harmonic frequency (203 cm^{-1}) is however smaller than the best prediction (217 cm^{-1}) in this work and than the experimental result. The IP and D_e calculated by MPBG employing an 8*s*6*p*3*d* basis are also in fair agreement with the coupled cluster (7*s*5*p*3*d*) predictions. On the other hand, although qualitatively correct, Balasubramanian's results do not compare with experiment as favorable as the MRD-CI and CC predictions presented herein.

Finally, it is important to note that the τ_1 diagnostics obtained for all CC calculations in this study are smaller than 0.023. The τ_1 diagnostic, defined as the norm of the t_1 CC amplitudes divided by the number of correlated electrons [28], is a measure of the importance of multi-reference effects in a single-reference framework. The present numerical results ($\tau_1 \leqslant 0.023$) indicate that the ground state of GaAs is adequately described by a single-reference correlated treatment.

4. Conclusion

The single-reference coupled cluster method provides an adequate framework for the theoretical description of the equilibrium bond-length, harmonic vibrational frequency, dissociation energy and ionization potential of the $^3\Sigma^-$ ground state of GaAs. In order to obtain accurate predictions of these molecular properties, large basis sets including f-type polarization functions must be employed. Correlation effects from $3d$-electrons are also of utmost importance. Consistent with relatively small τ_1 diagnostics, connected triple excitations are not found to be crucial for a correct qualitative description of this molecule.

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Note Added in Proof

Balasubramanian [29] has recently carried out CASSCF Second-Order CI (SOCI) calculations on the ground state of GaAs. The new results for r_e (2.60 Å), ω_e (215 cm^{-1}), D_e (1.7 eV), and IP (6.85 eV), are in much better agreement with experiment than the CASSCF-FOCI values reported in Table 1.