Influence of electron correlations on ground-state properties of III-V semiconductors

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Lattice constants and bulk moduli of eleven cubic III-V semiconductors are calculated using an \textit{ab initio} scheme. Correlation contributions of the valence electrons, in particular, are determined using increments for localized bonds and for pairs and triples of such bonds; individual increments, in turn, are evaluated using the coupled cluster approach with single and double excitations. Core-valence correlation is taken into account by means of a core polarization potential. Combining the results at the correlated level with corresponding Hartree-Fock data, we obtain lattice constants which agree with experiment within an average error of $-0.2\%$; bulk moduli are accurate to $+4\%$.

We discuss in detail the influence of the various correlation contributions on lattice constants and bulk moduli.

31.25.Qm,71.46.Gm,71.55.Eg

I. INTRODUCTION

Ground state properties of solids are most often calculated within the framework of density-functional theory (DFT), where the exchange and correlation contributions are determined within the local-density approximation (LDA)\cite{1}. These methods yield good results for lattice constants and bulk moduli but do not provide for many-body wave functions. Both, the influence of exchange and correlation are covered in an implicit way, thus, a systematic improvement towards the exact results appears to be difficult.

Hartree-Fock self-consistent-field (HF-SCF) calculations for solids\cite{2}, while lacking electron correlations as per its definition, have the merit of treating non-local exchange exactly. They supply a good starting point for subsequent correlation calculations provided correlations are not too strong. Infinite systems require the use of size-consistent approximations for electron correlations. In Ref.\cite{3} an approach based on cumulants was discussed which ensures size-consistency at any level of approximation. We use it here in order to work with local operators, i.e., local one- and two-particle excitations. These are best suited for describing the local correlation hole which the electrons carry with them. The matrix elements which appear in the calculation of the ground-state energy are evaluated using clusters instead of solids thereby applying an incremental method\cite{4}. The same method has previously been used to calculate ground-state properties of elementary semiconductors\cite{5} as well as the cohesive energy of cubic III-V compounds\cite{6}.

In the present paper we apply this method to eleven III-V compounds in zinc-blende structure and investigate the influence of electronic correlations on lattice constants and bulk moduli. In addition to the valence correlations the core polarization, which may have large influence on the bond lengths of molecules\cite{7}, is taken into account for the solid in a systematic way.

II. HARTREE-FOCK CALCULATION

Before discussing the influence of electron correlation effects in solids, reliable HF-SCF calculations are a necessary prerequisite. We performed HF ground-state calculations for the III-V compounds using the program package CRYSTAL92\cite{7}. The same basis sets and pseudopotentials as in Ref.\cite{5} are used\cite{8}.

The HF lattice constants have been determined from the minima of the HF ground-state energy curves in the following way. We varied the lattice constants in steps of $1\%$ of the experimental values and calculated six points of the potential curves in each case. The minima were evaluated from a quadratic fit to these points. A narrower spacing and higher order fits were tested but yielded only a marginal change in the position of the minimum and the curvature. The results for the HF lattice constants are listed in Table I.

The bulk moduli, which describe the response of the solid to a homogeneous pressure, have been evaluated at the experimental lattice constants\cite{9}. The HF values for the bulk moduli are listed in Table II.

III. CORRELATION EFFECTS

A. Core polarization

The description of core electrons by means of pseudopotentials implies a neglect of static and dynamic core polarization. The first part is an SCF effect, while the latter part is related to core-valence correlation. Especially if closed $d$ shells are described by pseudopotentials, the influence of the core polarization on lattice constants and bulk moduli is significant although the influence on cohesive energies is negligible. The computational effort
between the core and the valence electrons: 

\[ V_{\text{CPP}} = -\sum_{\lambda} \frac{1}{2} \alpha_\lambda \vec{f}_{\lambda} \cdot \vec{f}_{\lambda}; \]  

(1)

here \( \lambda \) numbers different cores, \( \alpha_\lambda \) is the corresponding dipole polarizability, and \( \vec{f}_{\lambda} \) is the field at the site of the core generated by valence electrons and surrounding cores:

\[ \vec{f}_{\lambda} = \sum_{i} \frac{r_{\lambda i}}{r_{\lambda i}^3} \left(1 - e^{-\delta_\lambda r_{\lambda i}^2}\right) - \sum_{\mu(\neq \lambda)} \frac{r_{\lambda \mu}}{r_{\lambda \mu}^3} \left(1 - e^{-\delta_\lambda r_{\lambda \mu}^2}\right); \]  

(2)

\( r_{\lambda i} \) is the distance between valence electron \( i \) and core \( \lambda \), \( N_V \) is the number of valence electrons. The cut-off parameter \( \delta_\lambda \) is necessary in order to remove the singularity of the dipole interaction at \( r_{\lambda i} = 0 \). We took the parameters \( \alpha_\lambda \) and \( \delta_\lambda \) from Ref. \( \text{[4]} \), where the CPP was adjusted in atomic calculations to the spectra of single-valence-electron ions.

In order to obtain information on the influence of CPP’s on solid-state properties, we choose a finite fragment of the zinc-blende structure – a \( X_4Y_4H_{18} \) cluster – where the dangling bonds are saturated with hydrogen atoms. The \( X—H \) and the \( Y—H \) distances, respectively, are optimized in CCSD calculations for \( XYH_6 \) cluster.\( ^5 \) For hydrogen we choose Dunning’s double-zeta basis\( ^6 \), without the \( p \) polarization function. For the other elements, large-core pseudopotentials in conjunction with corresponding \( (4s4p3d)/[3s3p1d] \) valence basis sets are used.\( ^3\)\( ^5\)

We first want to check the local character of the CPP. Test calculations for GaAs are performed in the following way. The CPP for Ga is only provided at the innermost Ga atom and the energy gain due to the CPP, \( \Delta E_{\text{CPP}}(\text{Ga}) \), is calculated at the HF-SCF level with the program package \textsc{Molpro99}.\( ^4 \) In the next step we provide the CPP only at the innermost As atom, and \( \Delta E_{\text{CPP}}(\text{As}) \) is determined. Providing the CPP’s at the inner Ga and the inner As atoms simultaneously, we finally calculate \( \Delta E_{\text{CPP}}(\text{Ga, As}) \), and we find that the non-additive part \( \Delta E_{\text{CPP}}(\text{Ga, As}) - (\Delta E_{\text{CPP}}(\text{Ga}) + \Delta E_{\text{CPP}}(\text{As})) \) is negligibly small.

With this knowledge in mind, we determine an approximation for the core-polarization energy of the solid per unit cell by calculating \( \Delta E_{\text{CPP}}(X, Y) \) in the \( X_4Y_4H_{18} \) cluster as described above. Varying all \( X—Y \) bonds in the \( X_4Y_4H_{18} \) cluster, we obtain the dependence of \( \Delta E_{\text{CPP}}(X, Y) \) on the lattice constant \( a \). The results at this level are listed in Table I for the lattice constants and in Table II for the bulk moduli; they include core-valence correlation (through the use of the CPP) but do not account for the coupling between core-valence and valence correlation, which is dealt with in the next subsection.

B. Valence correlations

As pointed out in the introduction, the matrix elements which appear in the calculations of the ground-state energy are obtained from replacing the solid by sufficiently large clusters. With these matrix elements the correlation contribution to the ground-state energy can be partitioned into a sequence of increments\( ^7 \) which are successively evaluated. The procedure and the computational details for the III-V compounds are described in Ref.\( ^8 \). In order to account for the valence/core-valence correlation-energy coupling, we included CPP’s on every \( X- \) and \( Y- \) atom and used the HF-SCF ground state with CPP as reference state for the correlation calculation. For the evaluation of the largest increments (one-bond and up to next-nearest-neighbour two-bond) the basis set was extended to \( (4s4p2d1f) \). Applying this method we determined the correlation energies as function of the lattice constant. The calculated lattice constants and bulk moduli are listed in Table I and Table II.

IV. RESULTS AND DISCUSSION

We have calculated the lattice constants and the bulk moduli for eleven cubic III-V semiconductors, at different theoretical levels. A HF treatment overestimates the lattice constants by up to 2\% , with the errors increasing for systems with heavier atoms. Apparently, it is due to the lack of electron correlations which describe the instantaneous motion of the electrons, that the structural minimum is found at larger volumes as compared to experiment. This is opposite to what is usually found for molecules composed of first- and second-row atoms in quantum-chemical calculations. There, the lack of non-dynamical correlation (left-right correlation), yields an artificial upwards shift of the potential-energy curve for large \( R \) and consequently leads to too short SCF bond lengths. Of course, this effect is also present in the solids considered in this paper, but apparently is overridden by dynamical correlation effects (cf. below). However, quite in common with quantum-chemical experience for molecular force constants, the bulk moduli are overestimated by up to 30\%, at the HF level. The materials seem to be harder (large bulk modulus) because the instantaneous answer of the electrons to pressure is neglected.

In the next step we take into account the core polarization. As described in Section III.A, the core polarization is neglected when using pseudopotentials. Pictorially speaking, the instantaneous deformation of the spherical cores in the field of the valence electrons is omitted. Modelling this effect with a core polarization potential, we achieve a significant reduction of the lattice constants (by up to -2\%). The calculated values for the bulk moduli decrease by up to 15\% depending on the materials.
(heavier atoms are easier to polarize).
The overall effect of the valence correlations determined with the method of local increments leads to a reduction of about 1% in the lattice constant and about 10% in the bulk modulus.
To get a deeper understanding of the nature of the interplay of the various correlation effects, we performed calculations for GaAs with different basis sets (see Table III). The interatomic (non-dynamical) part of the valence correlation energy is determined using a minimal \((4s4p)/(1s1p)\) basis set. It enlarges the lattice constant by more than 2%, because in the many-body wave function only excitations into anti-bonding orbitals are possible. Intra-atomic (dynamical) correlations (calculated with a larger than minimal basis) decrease the lattice constant because more low lying excitations are mixed into the interatomic many-body wave function within the enlarged configuration space. The electrons can avoid each other much better. Increasing the basis further (to \(4s4p2d1f\)) the intraatomic correlations are increased and lattice constants and bulk moduli are decreased.

A comparison between valence-correlation effects with and without CPP has also been made for GaAs (see Table III). This way, the coupling between valence and core-valence correlation can be investigated. While the interatomic part of the valence-correlation energy is virtually unchanged when including the CPP, the intraatomic one is reduced in the calculation with CPP. The reason for this effect, however, is not so much a reduction of dynamical valence correlation but rather a reduction of dynamical core-polarization when angular correlation around the atoms is introduced into the many-body wave function: angular correlation leads to a preference for valence electrons occupying opposite positions with respect to an atomic core so that their polarizing effect is reduced as compared to an independent-particle (uncorrelated) description. The major part of this effect comes from \(s\), \(p\) and \(d\) functions, the additional bond-length reduction due to \(f\) functions is nearly the same in the calculation with and without CPP.

For the lattice constants we reach a very good agreement with experiment. All calculated results are slightly too small (by \(-0.2\)% on the average), but they are within the error bars given by the pseudopotentials and the CPP's (\(\approx 0.03\) Å). We have checked the quality of the chosen basis set for the Ga—As bond length in GaAsH\(_6\). There, we see nearly no change (\(\leq 0.1\)% when extending the basis to an even larger one (6\(s6p3d2f1g\)). The average error of the calculated bulk moduli is about \(+4\)%.

For comparison, we have also listed in Table I and Table II results from the literature which have been obtained with LDA. Lattice constants are underestimated within the LDA treatment by up to \(2.8\)% . Bulk moduli mostly agree well with experiment.

V. CONCLUSION

We have determined the lattice constants and the bulk moduli of eleven cubic III-V semiconductors. At the HF-SCF level, the lattice constants are overestimated by up to 2\%, the bulk moduli by up to 30\%. A significant reduction towards the experimental values is obtained when applying core polarization potentials. Valence correlation has been calculated at the CCSD level, using the method of local increments. For the lattice constants two opposite trends are seen: interatomic correlations enlarge the lattice constant, while intraatomic ones decrease it. The overall trend is a reduction of the lattice constants, and the final results agree very well with experiment (average error \(\approx -0.2\)%). Valence correlations substantially decrease the bulk moduli, and again the agreement with experiment is remarkable good (average error \(\approx +4\)%). Due to the availability of many-body wave functions in our scheme, the influence of correlations on the lattice constants and the bulk moduli can be discussed in detail.

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### TABLE I. Lattice constants (in Å) at different theoretical levels (cf. text); deviations from experimental values are given in parentheses; the experimental values measured at room temperature have been extrapolated to zero Kelvin.

|        | $a_{\text{HF}}$       | $a_{\text{HF+CPP}}$       | $a_{\text{HF+CPP+corr}}$       | $a_{\text{LDA}}$       | $a_{\text{exp}}$ |
|--------|------------------------|---------------------------|--------------------------------|------------------------|-----------------|
| BP     | 4.5836 (+1.0%)         | 4.5679 (+0.7%)            | 4.5322 (-0.1%)                 | 4.4745 (-1.4%)         | 4.5373          |
| BAs    | 4.8276 (+1.1%)         | 4.8011 (+0.5%)            | 4.7644 (-0.3%)                 | 4.7770 (+0.0%)         | 4.777           |
| AlP    | 5.5348 (+1.3%)         | 5.5016 (+0.7%)            | 5.4398 (-0.5%)                 | 5.4215 (-0.8%)         | 5.4672          |
| AlAs   | 5.7405 (+1.5%)         | 5.6944 (+0.6%)            | 5.6428 (-0.3%)                 | 5.6215 (-0.7%)         | 5.6600          |
| AlSb   | 6.2606 (+2.1%)         | 6.1954 (+1.0%)            | 6.1307 (+0.0%)                 |                       | 6.1355          |
| GaP    | 5.5298 (+1.5%)         | 5.4636 (+0.3%)            | 5.4274 (-0.3%)                 | 5.3584 (-1.7%)         | 5.4459          |
| GaAs   | 5.7546 (+1.9%)         | 5.6730 (+0.4%)            | 5.6472 (+0.0%)                 | 5.5835 (-2.5%)         | 5.6485          |
| GaSb   | 6.2120 (+2.2%)         | 6.1034 (+1.0%)            | 6.0740 (+0.7%)                 | 5.9391 (-2.3%)         | 6.0806          |
| InP    | 5.9527 (+1.5%)         | 5.8559 (-0.2%)            | 5.8296 (-0.6%)                 | 5.7021 (-2.8%)         | 5.8666          |
| InAs   | 6.1524 (+1.6%)         | 6.0521 (+0.0%)            | 6.0437 (-0.2%)                 | 5.9019 (-2.5%)         | 6.0542          |
| InSb   | 6.5925 (+1.9%)         | 6.4717 (+0.0%)            | 6.4615 (-0.2%)                 | 6.3406 (-2.0%)         | 6.4719          |

### TABLE II. Bulk moduli (in Mbar) at different theoretical levels (cf. text); deviations from experimental values are given in parentheses.

|        | $B_{\text{HF}}$       | $B_{\text{HF+CPP}}$       | $B_{\text{HF+CPP+corr}}$       | $B_{\text{LDA}}$       | $B_{\text{exp}}$ |
|--------|------------------------|---------------------------|--------------------------------|------------------------|-----------------|
| BP     | 1.95 (+12%)            | 1.92 (+11%)               | 1.87 (+8%)                     | 1.73                   | 1.73            |
| BAs    | 1.62                   | 1.53                      | 1.51                           | 1.47                   | 1.48            |
| AlP    | 1.01 (+17%)            | 0.98 (+14%)               | 0.92 (+7%)                     | 0.86                   | 0.88            |
| AlAs   | 0.90 (+17%)            | 0.86 (+12%)               | 0.82 (+7%)                     | 0.82                   | 0.82            |
| AlSb   | 0.65 (+12%)            | 0.61 (+5%)                | 0.57 (-1%)                     | 0.58                   | 0.58            |
| GaP    | 1.10 (+21%)            | 0.98 (+8%)                | 0.93 (+2%)                     | 0.978 (+7%)            | 0.91            |
| GaAs   | 0.87 (+13%)            | 0.82 (+6%)                | 0.77 (0%)                      | 0.771 (+0%)            | 0.77            |
| GaSb   | 0.63 (+12%)            | 0.63 (+6%)                | 0.59 (+6%)                     | 0.794 (+43%)           | 0.56            |
| InP    | 0.79 (+10%)            | 0.71 (-1%)                | 0.66 (-8%)                     | 0.761 (+6%)            | 0.72            |
| InAs   | 0.74 (+28%)            | 0.69 (+19%)               | 0.64 (+10%)                    | 0.619 (+7%)            | 0.58            |
| InSb   | 0.58 (+26%)            | 0.52 (+11%)               | 0.48 (+4%)                     | 0.477 (+4%)            | 0.46            |

### TABLE III. Influence of correlations on lattice constants (in Å) of GaAs, employing different basis sets (cf. text); deviations from experimental values are given in parentheses.

|        | HF            | CCSD, min. basis | CCSD,3s3p1d | CCSD, 4s4p2d1f |
|--------|---------------|-----------------|-------------|----------------|
| $a_{\text{HF}}$       | 5.6730 (+0.4%) | 5.7910 (+2.5%)  | 5.7084 (+1.1%) | 5.6472 (+0.0%)  |
| $a_{\text{HF}}$       | 5.7546 (+1.9%) | 5.8810 (+4.1%)  | 5.7645 (+2.1%) | 5.7015 (+0.9%)  |