Quasiparticle energies for cubic BN, BP, and BAs

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(Received 9 November 1990)

Electronic excitation energies at the high-symmetry points Γ, X, and L are obtained for zinc-blende-structure BN, BP, and BAs in the GW approximation using a model dielectric function. A model for the static screening matrix makes use of the *ab initio* ground-state charge density and either experimental values or empirical estimates for ϵ_∞, the electronic contribution to the macroscopic dielectric constant. Wave functions from an *ab initio* local-density-approximation calculation with norm-conserving pseudopotentials are employed along with the self-consistent quasiparticle spectrum to obtain the energy-dependent one-particle Green function G. The minimum band gaps are found to be 6.3, 1.9, and 1.6 eV for BN, BP, and BAs, respectively, in close agreement with existing measurements of 6.1 and 2.0 eV for BN and BP, respectively. The BN direct band gap is predicted to be 11.4 eV versus the experimental value of 14.5 eV, and the BP direct band gap is predicted to be 4.4 eV versus 5.0 eV from experiment.

INTRODUCTION

There are currently little experimental data available on the electronic structure of the zinc-blende-structure materials BN, BP, and BAs. This situation exists despite the general interest in cubic BN and BP because of their extreme hardness and high thermal conductivity. To date, there have been no results from angle-resolved photoemission experiments available on these materials. However, some soft-x-ray-spectroscopy data is available, yielding band gaps and occupied-band widths.[1-5] There are also some optical studies that have been performed on BN,[6-9] BP,[10,11] and BAs.[12] There is less experimental information about BAs, since it is difficult to synthesize.[13] The optical studies have been limited mostly to the frequency dependence of the reflectivity or absorptivity; the studies on BP include the determination of the electro-luminescence and photoelectric response.[10] No firm identification of the optical features can be made on the basis of existing experiments alone; and attempts to identify structure in the reflectivity by analogy to SiC or by analogy to available theoretical results can provide only limited insight into the excitation spectra.

Unfortunately, the existing theoretical data cannot be relied upon to provide accurate estimates of excitation energies, since most band-structure calculations performed to date rely on the $X\alpha$ method,[14-18] the local-density approximation (LDA) to the density-functional theory,[19-24] or the Hartree-Fock approximation.[25] These theoretical methods can yield errors of up to several eV in band gaps or other excitation energies when compared to reliable experimental results. The Hartree-Fock approach neglects correlation entirely, and density-functional theory, upon which LDA is based, systematically underestimates band gaps.[26,27] The most recent *ab initio* LDA calculations yield a minimum band gap for BN ranging from 4.2 to 5.0 eV; the Hartree-Fock method yields a minimum band gap of 11.3 eV. Earlier empirical calculations[28-31] are limited by the paucity of experimental data.

Recent advances have made it feasible to perform *ab initio* calculations with enough quantitative accuracy to provide predictive information on the excitation energies of these compounds. These calculations employ the GW approximation[32] to properly include the effects of exchange and correlation on the quasiparticle energies. The GW approach has resulted in calculated band gaps with 0.1 eV accuracy[33-35] when a random-phase-approximation (RPA) dielectric matrix is used, or with 0.1-0.3 eV accuracy with use of an appropriate model dielectric matrix.[36-38] (The dielectric model requires a value for ϵ_∞ as an input parameter; the experimental value is used to avoid computing the dielectric constant explicitly. For this reason, and because the experimental lattice constants are used, the calculations are considered to be only partially *ab initio*.)

This paper examines the electronic excitation energies for high-symmetry points Γ, X, and L for the three boron compounds BN, BP, and BAs. The energies of the first 8 bands are calculated in the local-density and GW approximations. The effects of the relativistic spin-orbit interaction are included for BP and BAs. The results are compared to the existing experimental data, and the full theoretical data are tabulated for reference. The calculated minimum band gaps are in good agreement with existing experimental values based mainly on the onset of optical absorption. There are still significant discrepancies with the experimental data that are based on interpreting other features in the reflectivity.

THEORETICAL METHOD

The GW approximation starts with the exact formal expression for the one-particle excitation energies of an

interacting system of electrons in a crystal potential. These energies can be obtained as[32]

$$E^{qp}\Psi^{qp}(\mathbf{r}) = [\hat{T} + V_{ext}(\mathbf{r}) + V_C(\mathbf{r})]\Psi^{qp}(\mathbf{r})$$
$$+ \int d\mathbf{r}' \Sigma(\mathbf{r},\mathbf{r}';E^{qp})\Psi^{qp}(\mathbf{r}') , \quad (1)$$

where $\hat{T}$ is the kinetic-energy operator, V_C is the Hartree potential, V_{ext} the ionic potential, and the self-energy operator Σ includes the effects of exchange and correlation. When taken in the GW approximation, Σ depends only on the energy-dependent one-particle Green's function G and the dynamically screened Coulomb interaction W:[32]

$$\Sigma(\mathbf{r},\mathbf{r}';E) = i \int \frac{dE'}{2\pi} e^{-i\delta E'} G(\mathbf{r},\mathbf{r}';E-E')$$
$$\times W(\mathbf{r},\mathbf{r}';E) . \quad (2)$$

Vertex corrections are not included in this approximation.

In the approach taken here,[33] the additional quasiparticle approximation is made for the one-particle Green's function G; the quasiparticles are considered to have infinite lifetimes. It is also assumed that the LDA eigenfunctions adequately describe the quasiparticle wave functions.[33] Thus the Green's function becomes

$$G(E) = \sum_{n,\mathbf{k}} \frac{|n\mathbf{k}\rangle\langle n\mathbf{k}|}{E - E_{n\mathbf{k}}^{input} - i\eta} , \quad (3)$$

with $|n\mathbf{k}\rangle$ the LDA eigenfunctions, E^{input} the self-consistent quasiparticle energies, and η a negative infinitesimal for energies above the Fermi energy and a positive infinitesimal below. The use of the LDA wave functions as surrogates for the true quasiparticle wave functions simplifies the computation of excitation energies; specifically,

$$E_{n\mathbf{k}}^{qp} = E_{n\mathbf{k}}^{LDA} + \langle n\mathbf{k}|\Sigma(E_{n\mathbf{k}}^{qp})|n\mathbf{k}\rangle - \langle n\mathbf{k}|V^{LDA}|n\mathbf{k}\rangle . \quad (4)$$

That is, the contribution of the LDA exchange and correlation to the energy of the LDA eigenstate is simply replaced by the expectation of the energy-dependent self-energy operator. These approximations have been shown to be highly reliable in the past,[33,39] and the quantitative success obtained here suggests that they are reasonable for the present class of materials as well.

The screened Coulomb interaction in Eq. (2) is given by

$$W(\mathbf{r}_1,\mathbf{r}_2;\omega) = \int d\mathbf{r}_3 \epsilon^{-1}(\mathbf{r}_1,\mathbf{r}_3;\omega)v(\mathbf{r}_3,\mathbf{r}_2) , \quad (5)$$

with v the bare Coulomb interaction. This quantity is also approximated, since a complete evaluation is impractical. Typically, the static dielectric response matrix is obtained by either a model or a linear-response perturbation calculation in the random-phase approximation (RPA), and the static matrix is then extended to finite frequency with a generalized plasmon-pole approximation. An effective plasmon mode is fitted with two frequency moments to obey the Kramers-Kronig and f-sum rules.[33] The static screening and ground-state charge density are the only information needed. This basic method has been successfully applied to a number of diamond-structure

(C, Si, and Ge) and zinc-blende-structure material AlAs, AlP, AlSb, GaAs, GaP, GaSb, InAs, InP, and InSb.[36-38]

There are essentially two different plasmon-pole schemes that have been used in GW calculations. The original plasmon-pole method due to Hybertsen and Louie[33] and Zhang et al.[35] assigns one plasmon mode per element in the matrix. This is referred to as the generalized plasmon-pole method (GPP). It yields N^2 plasmon modes for an $N \times N$ dielectric matrix. Another is the dielectric band-structure (DBS) approach of von der Linden and Horsch,[40] which is the method used in this paper (and in Ref. 38). In this approach the dielectric matrix is put in Hermitian form and diagonalized;[41] each eigenfunction is assigned one plasmon mode; thus a $N \times N$ dielectric matrix will have N plasmon modes. The two methods yield equivalent results for the self-energy for the semiconductors considered.

A suitable static dielectric matrix is needed as a starting point for either plasmon-pole approach. In this paper the static screening is obtained by using a model based on the ground-state charge density and the macroscopic dielectric constant. The long-range screening is fitted to the input ϵ_∞, and the local fields are included through the variation in the electron density.[36-38] The value for ϵ_∞ is taken as 4.5 for BN from the Landolt-Börnstein tables;[13] 10.8 for BP from the experimental value of ϵ_0, the optical-phonon frequencies, and the LST relations;[13] and 10.4 for BAs derived from the empirical relation due to Philips and van Vechten:

$$\epsilon_\infty = 1 + \frac{(\hbar\omega_p)^2}{E_h^2 + C^2} , \quad (6)$$

with ω_p the bulk plasmon frequency of 20.1 eV, E_h the heteropolar gap of 6.55 eV, and C the homopolar gap of 0.38 eV.[42] This estimate for BAs should be accurate. The Phillips–van Vechten relation and the empirical parameters are reliable for BN and BP, yielding values for ϵ_∞ of 5.0 and 9.5, respectively. In practice, the final quasiparticle energies are insensitive to the precise value of ϵ_∞ used.[36]

ACCURACY OF THE MODEL

The accuracy of the quasiparticle energies derived from the model dielectric matrix depends on the material being studied. As a result, it is important to examine earlier GW calculations to provide an estimate of the anticipated accuracy for BN, BP, and BAs when using the DBS formalism and a model dielectric function. Tables I and II show the LDA and GW results as well as the available experimental data for diamond and Si. The percentage errors between the calculated minimum band gaps and the experimental values are essentially the same for diamond and silicon. For example, the calculated band gaps of silicon using the model dielectric matrix agree well with experiment and with the RPA results, but the diamond direct band gaps differ from experiment by 0.3 for $\Gamma_{15'v}$-Γ_{15c} and up to 0.5 eV for X_{4v}-X_{1c}. (We note that the minimum band gap of diamond is actually better

TABLE I. Diamond excitation energies (in eV) at high-symmetry points from LDA and two GW calculations and experiment. The GW calculations are identified by the method used to obtain the static response and the plasmon-pole approximation used to obtain frequency-dependence. The model-DBS results are from a dielectric band-structure plasmon-pole formalism with a model dielectric matrix (Ref. 38). The RPA GPP results are from the generalized plasmon-pole method with a calculated RPA dielectric matrix (Ref. 33). The experimental data are from Ref. 13 unless otherwise noted.

	LDA	model-DBS	RPA-GPP	Expt.
$\Gamma_{25'}^v \to \Delta_1^c$	3.9	5.5	5.6	5.48
$\Gamma_{25'}^v \to \Gamma_{15}^c$	5.5	7.6	7.5	7.3
$\Gamma_1^v \to \Gamma_{25'}^v$	21.7	24.4	23.0	24.2,21±1[a]
$\Gamma_{25'}^v \to \Gamma_2^c$	13.1	15.3	14.8	15.3±0.5[a]
$L_{3'}^v \to L_1^c$	11.5	13.6		12.5,16.3
$L_{3'}^v \to L_3^c$	11.2	13.9		12.0
$X_4^v \to X_1^c$	10.8	13.1	12.9	12.5,12.6
$L_2^v \to \Gamma_{25'}^v$	15.8	18.2	17.3	15.2±0.3[a]
$L_1^v \to \Gamma_{25'}^v$	13.6	15.2	14.4	12.8±0.3[a]
$\Gamma_{25'}^v \to L_{2'}^c$	15.2	18.2	17.9	20±1.5[a]

[a]Reference 45.

estimated with the model screening than with the RPA; this is also true for the GPP-model calculation.[36])

It is important to note the strong directional **k** dependence of the quasiparticle corrections to the LDA energies that occur in diamond, a wide-band-gap material with strong local-field effects. This can be seen by comparing the LDA and quasiparticle gaps Γ_{15v}-X_{1c} versus Γ_{15v}-L_{1c} (Table I). The Γ_{15v}-X_{1c} LDA gap is increased

TABLE II. Silicon excitation energies (in eV). The LDA and QP-model results are from Ref. 38, the RPA results are from the GW calculation of Ref. 33, and the experiment is from Ref. 13, unless otherwise noted.

	LDA	model-DBS	RPA-GPP	Expt.
$\Gamma_{25'}^v \to \Delta_1^c$	0.55	1.16	1.29	1.17
$\Gamma_{25'}^v \to \Gamma_{15}^c$	2.57	3.36	3.35	3.4[a]
$\Gamma_{25'}^v \to \Gamma_2^c$	3.38	4.21	4.08	4.19
$\Gamma_1^v \to \Gamma_{25'}^v$	11.92	12.45	12.04	12.5±0.6
$X_4^v \to \Gamma_{25'}^v$	2.86	3.07	2.99	2.9,[b]3.3±0.2[c]
$\Gamma_{25'}^v \to X_1^c$	0.69	1.29	1.44	1.3[d]
$L_{2'}^v \to \Gamma_{25'}^v$	9.57	10.08	9.79	9.3±0.4
$L_1^v \to \Gamma_{25'}^v$	6.96	7.37	7.18	6.7±0.2
$L_{3'}^v \to \Gamma_{25'}^v$	1.20	1.29	1.27	1.2±0.2,1.5[e]
$\Gamma_{25'}^v \to L_1^c$	1.53	2.26	2.27	2.1,[f]2.4±0.15[g]
$\Gamma_{25'}^v \to L_3^c$	3.37	4.19	4.24	4.15±0.1[g]
$L_{3'}^v \to L_1^c$	2.73	3.55	3.54	3.45[a]
$L_{3'}^v \to L_3^c$	4.57	5.49	5.51	5.50[a]

[a]Reference 46.
[b]Reference 47.
[c]Reference 48.
[d]Estimated from indirect gap and longitudinal mass (Ref. 33).
[e]Reference 49.
[f]Reference 50.
[g]Reference 51.

by 1.5 eV; the Γ_{15v}-L_{1c} LDA gap increases by 2.3 eV.[38] Additionally, the quasiparticle correction can depend strongly on the symmetry of the states at a single **k** point. The effect is most prominent for the first two conduction bands of diamond at L (see Table I). Here, the order of the two quasiparticle bands is reversed from the LDA. The LDA results put the twofold-degenerate L_{3c} states below the nondegenerate L_{1c} state, while the GW correction [Eq. (4)] yields a relative shift of 0.6 eV between the two states that reverses their order. The GW results are in disagreement with the interpretation of the experimental; however, this interpretation is not always straightforward. The lower two X conduction bands in BAs also change position; the LDA puts the X_{1c} state marginally above the X_{3c},[20] but the GW results put X_{1c} some 0.07 eV lower. In this case the relative shift of 0.07 eV is well within the error bars. It is important to note that the shift is too small, anyway, to affect the character of the conduction-band minimum along Δ.

Note that the self-consistent quasiparticle spectrum is required in the Green's function $G(E)$ in Eq. (3). In principle, the spectrum E_{nk}^{input} that is used in $G(E)$ should be obtained by iteratively solving Eq. (1) for each **k** point and band n. In practice, E_{nk}^{input} is obtained from the conduction and valence bands from an isotropic adjustment of the LDA spectrum linearly fitted to the calculated GW spectrum from the previous iteration:

$$E_v^{\text{input}} = (1 + A_v)E_v^{\text{LDA}} + B_v , \tag{7}$$

$$E_c^{\text{input}} = (1 + A_c)E_c^{\text{LDA}} + B_c . \tag{8}$$

The fit for A and B is made to the direct band gaps at Γ and L for diamond and the band gaps at Γ and X for BN, BP, and BAs. This is a more sophisticated approach to self-consistency than a scissors operator, and it requires self-consistent quasiparticle energies at only two (high-symmetry) **k** points instead of at all points in the Brillouin zone.

However, the directional **k** dependence of the fitted energy surface E_{nk}^{input} differs slightly from the final, self-consistent spectrum from Eq. (1) even for bands close to the band gap. For example, the input spectrum differs from the final, self-consistent one by 0.6 eV for diamond at X_{1c} and by 0.7 eV for BN at L_{1c} (the fits for Si, BP, and BAs are much closer). The GW results for diamond are still reliable; so this approximation should be acceptable for BN, as well.

The higher-energy excitations are intrinsically less reliable in all of the materials studied, regardless of the form of the static dielectric function, (i.e., perturbative or model). The assumption of infinite lifetimes for the quasiparticles is invalid for excitation energies much greater than the gap. The interpretation of experiment in terms of specific single-particle excitations may also be less reliable for high energies (note the discrepancy for the Γ-to-L excitations in Table I).

Based on these trends, the uncertainty in the GW results can be estimated to be 0.2 eV for the low-lying excitations in BN and 0.1 eV for BP and BAs. This is so because BN is the III-V analog of diamond, a wide-band-

gap material, while BP and BAs are both more similar to silicon.

RESULTS AND CONCLUSIONS

The results for the LDA and GW calculations for BN, BP, and BAs are listed in Tables III–V along with the existing experimental data. The scalar-relativistic LDA energies are obtained with a plane-wave basis using essentially the same norm-conserving pseudopotentials as those in Ref. 20. The experimental lattice constants are used,[13] and the plane-wave bases are cut off at 55 Ry for BN, slightly less than 20 Ry for BP, and 22 Ry for BAs. The basis sizes are approximately 550, 250, and 320 plane waves for the three compounds, respectively; this leads to LDA eigenvalues that are typically converged to within 0.05 eV. The symmetry identifications for the states in BN and BP are taken from Ref. 20, since the underlying LDA calculations performed here are virtually identical.

The calculated spin-orbit splittings are less than 0.05 eV for BP, and so they are not considered here; the results in Table IV are the scalar-relativistic values. The effect is slightly larger in BAs; therefore the results presented in Table V are fully relativistic. The spin-orbit splittings are calculated for BAs following the method of Ref. 43. The scalar-relativistic LDA spectrum is used in defining the unperturbed Hamiltonian, and the spin-orbit interaction is treated as a perturbation among the first 50 bands. The results of the spin-orbit perturbation are largely independent of whether the LDA or GW spectrum is used. The symmetries of the BAs states are for the double group of the zinc-blende-structure space group T_d^2 ($F\bar{4}3m$; the underlying scalar-relativistic symmetries are again from Ref. 20). Most of the symmetry identifications for the double group are straightforward, since most of the scalar-relativistic bands correspond to one-dimensional representations. The spin-orbit splitting of the X_5 and L_3 states is analyzed in the Appendix.

The band-gap corrections for BN show the same direc-

TABLE III. BN excitation energies from LDA and GW methods compared to existing experimental data.

	LDA	GW	Expt.
E_g	4.3	6.3	6.0 ± 0.5,[a]6.4 ± 0.5,[b]6.1 ± 0.2[c]
$\Gamma_{15}^v\to\Gamma_{15}^c$	8.6	11.4	14.5[d]
Lower-valence-band width			
$\Gamma_1^v\to K_1^v$	5.9	6.3	5.2[e]
Upper-valence-band width			
$L_1^v\to\Gamma_{15}^v$	10.6	12.1	15.4 ± 0.5,[a]13.5[e]
Total valence-band width			
$\Gamma_1^v\to\Gamma_{15}^v$	20.1	23.1	<22.0[a]

[a]X-ray emission (Ref. 1).
[b]Transmittance (Ref. 8).
[c]Reflectance-transmittance (Ref. 9).
[d]Reflectance (Ref. 6).
[e]X-ray emission (Ref. 2).

TABLE IV. BP excitation energies compared to experiment.

	LDA	GW	Expt.
E_g			
$\Gamma_{15}^v\to\Delta_{min}^c$	1.2	1.9	2.02 ± 0.05,[a]2.1 ± 0.2,[b]2.0[c]
Total valence-band width			
$\Gamma_1^v\to\Gamma_{15}^v$	15.5	16.8	16.5 ± 0.5[b]
$\Gamma_{15}^v\to\Gamma_{15}^c$	3.4	4.4	5.0[c]
$X^v\to X^c$	5.4	6.5	6.9[c]
$L^v\to L^c$	5.4	6.5	8.0[c]

[a]Reflectivity, electroluminescence (Ref. 11).
[b]X-ray emission (Ref. 4).
[c]Reference 10.

tional dependence that was seen for diamond, although the behavior is less pronounced. The Γ_{15v}-X_{1c} gap increases by 2.0 eV versus an increase of 2.3 eV for the Γ_{15v}-L_{1c} gap and an increase of 2.8 eV for the Γ_{15v}-Γ_{15c} gap (Table III). There is a similar small deviation from a scissors-operator opening of the Γ,X,L gaps in BP and BAs. The state dependence of the band-gap correction is only a few tenths of an eV, as in the case of silicon.

The calculated minimum band gap for BN is found to be 6.3 with an uncertainty of ±0.2 eV. The minimum band gaps are found to be 1.9 ± 0.1 eV and 1.6 ± 0.1 eV for BP and BAs, respectively. These results are in good accord with existing experimental data of 6.1 ± 0.2 eV for BN (Ref. 11) and 2.02 ± 0.05 eV (Ref. 9) for BP. The only available experimental data for BAs are probably not reliable; they yield a value of 0.67 eV for the minimum band gap.

The calculated minimum band gaps for BN and BAs have been estimated from the energy of the conduction band at X and the difference between that point and the conduction-band minima along Δ (at approximately $0.8X$ for both BP and BAs). The difference in the LDA energies between X_c and Δ_c^{min} is scaled by the parameter $1+A_c$ [see Eq. (7)], which is 1.2 for BP and BAs. Roughly speaking, the LDA conduction band is rigidly shifted upwards and then broadened by 20% in obtaining the GW band gap. The actual, self-consistent, GW conduction-band minimum was not calculated. This interpolation should be accurate to better than 0.1 eV, since the total difference in energy between X_c and Δ_c^{min} is at most a few tenths of an electron volt. A similar caveat applies to the lower-valence-band width of BN, which is from Γ to K. The GW energy for the state at K is inter-

TABLE V. BAs excitation energies compared to experiment.

	LDA	GW	Expt.
E_g			
$\Gamma_{15}^v\to\Delta_{min}^c$	1.1	1.6	0.67[a]
$\Gamma_{15}^v\to\Gamma_{15}^c$	3.3	4.2	1.46[a]
$\Gamma_1^v\to\Gamma_{15}^v$	15.5	16.7	16[b]

[a]Tentative identifications (Ref. 12).
[b]X-ray emission; estimated from Fig. 4, Ref. 5.

TABLE VI. Scalar-relativistic BN energies at high-symmetry points in the LDA and GW approximations (in eV). The energy of the valence-band maximum is set to zero in both calculations. Symmetry labels are from Ref. 20.

	LDA	GW		LDA	GW		LDA	GW
Γ_1^c	10.3	12.6	X_5^c	17.7	21.9	L_1^c	15.0	18.5
Γ_{15}^c	8.6	11.4	X_5^c	17.7	21.9	L_3^c	10.5	13.4
Γ_{15}^c	8.6	11.4	X_3^c	9.1	11.3	L_3^c	10.5	13.4
Γ_{15}^c	8.6	11.4	X_1^c	4.3	6.3	L_1^c	10.1	12.4
Γ_{15}^v	0.0	0.0	X_5^v	−4.9	−5.5	L_3^v	−1.9	−2.2
Γ_{15}^v	0.0	0.0	X_5^v	−4.9	−5.5	L_3^v	−1.9	−2.2
Γ_{15}^v	0.0	0.0	X_3^v	−8.8	−10.2	L_1^v	−10.6	−12.1
Γ_1^v	−20.1	−23.1	X_1^v	−14.3	−16.9	L_1^v	−15.7	−18.5

polated from the value at X and the LDA difference between X and K by scaling with $1 + A^v = 1.13$.

The GW direct band gaps are obtained for all three materials by explicit calculation at Γ, X, and L. They differ from the experimental estimates by significant amounts, most probably because the experimental values are estimates from analyzing structure in the frequency-dependent reflectivity without detailed theoretical calculations. The GW direct band gaps for BN are 11.4, 11.8, and 14.6 eV at Γ, X, and L, respectively; these are increased from the LDA values by some 2.4–2.8 eV. The GW direct band gap differs substantially from the experimental direct band gap of 14.5 eV at Γ extracted from reflectivity measurements.[6] The direct band gaps for BP are 4.4, 6.5, and 6.5 eV at Γ, X, and L, respectively; they are all approximately 1.0 eV larger than the LDA values. The experimental direct band gaps for BP are estimated to be 5.0 eV at Γ, 6.9 eV at X, and 8.0 eV at L—all estimated from reflectivity data.[10] These are inferred by analogy to SiC. The BP direct band gaps are both 6.5 eV at X and L in the GW calculation. This implies that the distinct feature assigned to the direct transition at L is probably due to some other process. However, there are no obvious candidate transitions at the three high-symmetry points; a possible identification would require a complete GW joint density-of-states calculation.

The energies of the lowest eight bands are presented for all three boron compounds in Tables VI–VIII. The self-energy and V^{LDA} expectations of Eq. (4) are computed using the LDA eigenfunctions, as was already mentioned. The operators for the exchange and correlation contributions to the self-energy are calculated up to

plane-wave cutoffs of 31, 20, and 20 Ry for BN, BP, and BAs, respectively. (The LDA potential is evaluated up to a cutoff of twice the maximum magnitude of plane-wave components for the wave functions. Thus, there is effectively no truncation of the LDA potential.) The Green's function of Eq. (3) is truncated at 150 bands for BN and 120 bands for BP and BAs when computing the correlation contribution to Σ.

It is evident from these results that the minimum band gaps of BN and BP have been reliably estimated from the experimental optical absorption. However, the direct band gaps and other excitation energies must be estimated from structure in the optical response versus frequency. The accuracy of the resulting experimental quotations depends on the correct identification of features in, e.g., the reflectivity with particular transitions between band states. As a result, the GW results may be more reliable estimates than the experimental direct band gaps. Furthermore, there are no experimental excitation energies other than the minimum band gaps, a few direct band gaps, and some occupied-band widths. The additional results contained in Tables VI–VIII are thus the best currently available data known to us on the electronic excitation spectra of these boron compounds.

ACKNOWLEDGMENTS

TABLE VII. Scalar-relativistic BP energies at high-symmetry points (in eV).

	LDA	GW		LDA	GW		LDA	GW
Γ_1^c	7.2	8.4	X_5^c	11.0	13.8	L_1^c	10.0	11.2
Γ_{15}^c	3.4	4.4	X_5^c	11.0	13.8	L_3^c	4.7	5.8
Γ_{15}^c	3.4	4.4	X_3^c	1.6	2.4	L_3^c	4.7	5.8
Γ_{15}^c	3.4	4.4	X_1^c	1.3	2.0	L_1^c	3.7	4.6
Γ_{15}^v	0.0	0.0	X_5^v	−4.1	−4.5	L_3^v	−1.7	−1.9
Γ_{15}^v	0.0	0.0	X_5^v	−4.1	−4.5	L_3^v	−1.7	−1.9
Γ_{15}^v	0.0	0.0	X_3^v	−8.6	−9.5	L_1^v	−9.1	−9.9
Γ_1^v	−15.5	−16.8	X_1^v	−10.5	−11.5	L_1^v	−12.0	−13.2

TABLE VIII. Fully relativistic BAs energies at high-symmetry points (in eV). The scalar-relativistic symmetries are listed first, followed by the double-group notation. Note the crossing of the lowest LDA conduction band, X_3, with the nearby X_1 state.

	LDA	GW		LDA	GW		LDA	GW
$\Gamma_1^c \rightarrow \Gamma_6^c$	4.5	5.5	$X_5^c \rightarrow X_6^c$	11.4	13.1	$L_1^c \rightarrow L_6^c$	8.8	9.8
$\Gamma_{15}^c \rightarrow \Gamma_8^c$	3.3	4.2	$X_5^c \rightarrow X_7^c$	11.2	12.9	$L_3^c \rightarrow L_4^c, L_5^c$	4.8	5.7
$\Gamma_{15}^c \rightarrow \Gamma_8^c$	3.3	4.2	$X_1^c \rightarrow X_6^c$	1.38	1.86	$L_3^c \rightarrow L_6^c$	4.7	5.6
$\Gamma_{15}^c \rightarrow \Gamma_7^c$	3.1	4.0	$X_3^c \rightarrow X_7^c$	1.36	1.93	$L_1^c \rightarrow L_6^c$	2.6	3.3
$\Gamma_{15}^v \rightarrow \Gamma_8^v$	0.00	0.00	$X_5^v \rightarrow X_6^v$	-4.1	-4.5	$L_3^v \rightarrow L_4^v, L_5^v$	-1.8	-2.0
$\Gamma_{15}^v \rightarrow \Gamma_8^v$	0.00	0.00	$X_5^c \rightarrow X_7^v$	-4.2	-4.6	$L_3^v \rightarrow L_6^v$	-1.9	-2.1
$\Gamma_{15}^v \rightarrow \Gamma_7^v$	-0.22	-0.22	$X_3^v \rightarrow X_7^v$	-8.6	-9.5	$L_1^v \rightarrow L_6^v$	-8.8	-9.7
$\Gamma_1^v \rightarrow \Gamma_6^v$	-15.5	-16.7	$X_1^v \rightarrow X_6^v$	-11.3	-12.2	$L_1^v \rightarrow L_6^v$	-12.6	-13.6

APPENDIX: FULLY RELATIVISTIC ZINC-BLENDE SYMMETRIES

The symmetry identifications for the scalar-relativistic states in BN, BP, and BAs have already been made in Ref. 20 for a LDA calculation. The spin-orbit correction was not considered in this reference, since it is relatively unimportant, except for BAs, and there are no experimental data on the BAs splittings. Here, the spin-orbit splitting in BAs is included, since it is found to be significant compared with the expected accuracy of the GW model.

Some additional analysis is required to obtain the fully relativistic symmetries of the BAs states given the scalar-relativistic identifications. The basic group theory of the zinc-blende-structure states at Γ, X, and L is found in Ref. 44. All of the fully relativistic bands are at least twofold degenerate at these high-symmetry points, and so, the double-group representation follows uniquely from the single group for all scalar-relativistic states that are twofold degenerate. The identification is nontrivial if there is a spin-orbit splitting of a scalar-relativistic degeneracy. In that case the different split states need to be distinguished.

Only the Γ_{15}, X_5, and L_3 scalar-relativistic states are split upon the inclusion of spin-orbit interactions. The Γ_{15} sixfold complex splits into the twofold-degenerate Γ_7 and fourfold-degenerate Γ_8, and the identification is trivial.

The second case to be considered is for the L_3 fourfold-degenerate states which split upon inclusion of the spin. The L_3 states split into L_4, L_5 (which are degenerate with each other), and the two-fold-degenerate L_6. The two states are distinguished by examining **k** along the [111] direction near L. Λ_6 is twofold degenerate, and Λ_4 and Λ_5 are nondegenerate. Thus, the continuation of the bands along Λ determines the symmetries. The LDA eigenvalues were obtained from a point at 0.999 from Γ to L, and the degeneracies there unambiguously identify the symmetries of the states at L.

The final state to consider, X_5, is also fourfold degenerate. It splits into X_6 and X_7 representations which are distinguished by their behavior under an operation $I \times C_{4\parallel}$,[44] with the C_4 on an axis parallel to the X direction. If the representative X point is taken for **k** along the $\hat{z}$ direction, the states are

$$X_6 = Y_{1,1} \downarrow; \quad Y_{1,-1} \uparrow \tag{A1}$$

and

$$X_7 = Y_{1,1} \uparrow; \quad Y_{1,-1} \downarrow . \tag{A2}$$

$Y_{1,\pm1}$ are the standard Y_{lm} angular momentum functions, and spin is quantized parallel to **k**. This definition of X_6 and X_7 fixes the sense of the rotation around the $\hat{z}$ axis, $C_{4\parallel}$.

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