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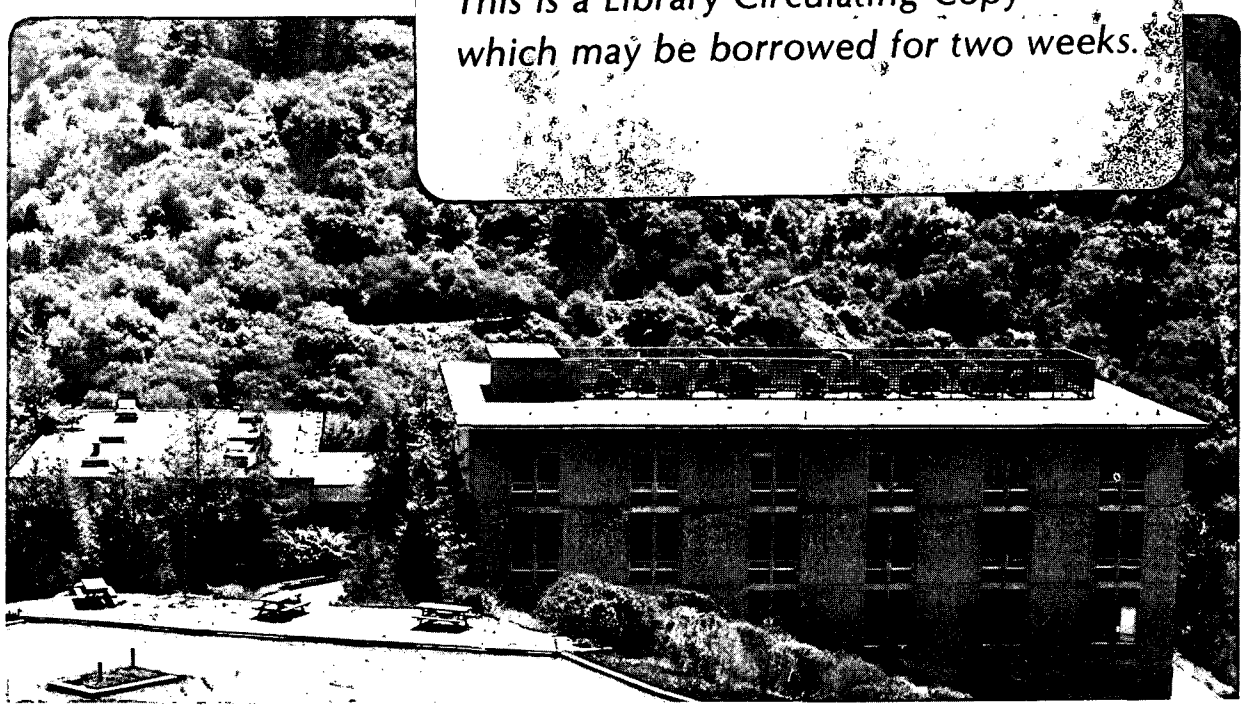

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LBL-23257

THEORY OF QUASIPARTICLE ENERGIES: BAND GAPS AND EXCITATION SPECTRA IN SOLIDS

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Abstract

A first-principles theory for the band gaps and electronic excitation energies in crystals is described. Optical and photoemission spectra are properly interpreted as transitions between quasiparticle states of the many-electron system. The theory requires adequate treatment of the Coulomb interaction between the electrons including exchange and dynamical correlation effects. The nonlocal energy-dependent electron self-energy operator is evaluated from first principles using the full dielectirc matrix and the dressed Green's function. Quasiparticle energies for materials covering a wide range of metallicity and ionicity are presented. With no empirical input, the calculated band gaps, optical transition energies, and band dispersions are all within a few percent of experimental values. For semiconductors and insulators, we find that local field effects in the screening of the Coulomb interaction and dynamical renormalization are both crucial for accurate results. The present method also extends beyond the case of bulk crystals, e.g., to surfaces. Results on the surface state energies of the Ge(111):As and Si(111):As surface are discussed and compared with experiment.

I. INTRODUCTION

The interpretation of the electronic excitation spectra of materials such as those measured in transport, optical, and photoemission experiments requires the concept of quasiparticles, the particle-like excitations of an interacting many-electron system. A major difficulty in calculating the quasiparticle properties has been in providing an adequate description of the dynamical correlations of the electrons in a real solid.[1] The development of a quantitative and predictive theory is therefore of longstanding interest and of major importance both from the point of view of many-body theory and for practical studies of excited-state properties of solids.

Most modern ab initio electronic structure calculations for solids are based on the density functional formalism [2] which in principle provides an exact description of the ground state of a many-electron system. Indeed, within the local density approximation (LDA), calculations of this kind have had considerable success for many ground-state properties of real materials.[3,4] However, the eigenvalues from the associated single-particle equations in this theory are not interpretable as quasiparticle energies although this is often done for lack of alternatives. For semiconductors and insulators, the experimental energy gaps are typically underestimated by 30-100% in the LDA giving rise to the so-called "band-gap" problem. This is illustrated in Table I.[5,6] For Ge, a relativistic LDA calculation even yielded a semimetallic band structure. Similarly, large discrepancies in the band gaps and band widths have been observed for the metals.[7,8] Hartree-Fock eigenvalues are even less satisfactory.

Although for the special case of the minimum gap of insulators, the band gap is shown to be obtainable by adding an explicit correction to the Kohn-Sham value, [9] it is now clear that direct quasiparticle calculations

are required for proper account of the excited-state properties of materials in general. This situation has stimulated much recent theoretical activities, and several many-body approaches have been proposed.[10-14]

In this paper, we give an overview of some results from a recently developed first-principles theory of quasiparticles.[10] The approach is based on evaluation of the electron self-energy to first order in the dynamically screened Coulomb interaction, the GW approximation.[1] The full dielectric matrix is used so that both the effects of local fields and dynamical screening are included. Successful applications [10] have been made to the quasiparticle band structure of the semiconductors and insulators including diamond, Ge, and Si as well as the ionic crystal LiCl resolving the band-gap problem and other discrepancies in excitation spectra between theory and experiment. The method has also been extended to provide a first-principles description of surfaces.[15] Finally, our work on the alkali metals [16] show that the large bandwidth reduction observed in recent angle-resolved photoemission experiments in Na [8] can be explained by the quasiparticle results.

The remainder of the paper is organized as follows. The next section presents some aspects of the theory. This is followed by a discussion of applications with emphasis on the semiconductors and insulators. Finally, a brief summary and conclusions are given.

II. QUASIPARTICLE THEORY

The quasiparticle energies and wavefunctions are given by [1]

$$(T + V_{ext} + V_H)\psi_{n\vec{k}}(\vec{r}) + \int d\vec{r}'\Sigma(\vec{r},\vec{r}';E_{n\vec{k}})\psi_{n\vec{k}}(\vec{r}') = E_{n\vec{k}}\psi_{n\vec{k}}(\vec{r}) \ . \quad (1)$$

Here, T is the kinetic energy operator, V_{ext} is the external potential due to the ions, V_H is the Hartree potential, and the exchange-correlation contributions are included in the self-energy operator Σ which, in general,

is nonlocal, energy-dependent, and non-Hermitian with the imaginary part giving the lifetime of the quasiparticles. Σ can be systematically expanded in a series in terms of the screened Coulomb interaction $W = \varepsilon^{-1}V$ and the fully dressed Green's function G as shown by Hedin [1] in 1965. The advantage of an expansion in W over one in terms of the bare Coulomb interaction V is that W, being a screened quantity, is much weaker than V and should lead to a rapidly convergent series.

Our work is based on a first-order expansion for Σ (the GW approximation),

$$\Sigma(\vec{r},\vec{r}';E) = i \int (d\omega/2\pi)e^{-i\delta\omega}G(\vec{r},\vec{r}';E-\omega)W(\vec{r},\vec{r}';\omega) \qquad (2)$$

where $\delta = 0^+$. Thus, the required inputs to evaluate Σ are the full interacting Green's function for which we adopt a quasiparticle approximation

$$G(\vec{r},\vec{r}';E) = \sum_{n\vec{k}} \frac{\psi_{n\vec{k}}(\vec{r})\psi^*_{n\vec{k}}(\vec{r}')}{E - E_{n\vec{k}} - i\delta_{n\vec{k}}} \qquad (3)$$

and the dynamically screened Coulomb interaction,

$$W(\vec{r},\vec{r}';\omega) = \Omega^{-1} \int d\vec{r}''\varepsilon^{-1}(\vec{r},\vec{r}'';\omega)V(\vec{r}'' - \vec{r}') \qquad (4)$$

where ε^{-1} is the time-ordered dielectric matrix. Our approach [10] is to make the best possible approximations for G and W separately, calculate Σ, and then obtain the quasiparticle energies. Note that the self-energy operator must be obtained together with G in a self-consistent fashion.

In the calculations, the electron Green's function G is constructed initially with use of the LDA eigenfunctions and eigenvalues and is subsequently updated with the quasiparticle spectrum from Eq. (1). This self-consistent iteration process for G is important for quantitative results in many cases, e.g., the large gap insulators and the alkali metals. The quasiparticle wavefunctions, on the other hand, are remarkably close to the initial LDA wavefunctions.[10] Evaluation of the screened

Coulomb interaction requires the full dielectric matrix, $\varepsilon^{-1}(\vec{r},\vec{r}';\omega)$, or in Fourier space, $\varepsilon^{-1}_{\vec{G}\vec{G}'}(\vec{q},\omega)$, where $\vec{G}$ and $\vec{G}'$ are the reciprocal lattice vectors. To simplify the calculations, we evaluate the dielectric matrix in two steps. The static dielectric matrix $\varepsilon_{\vec{G}\vec{G}'}(\vec{q},\omega=0)$, being a ground-state property, is obtainable within the (local) density functional theory. It is calculated from first principles using the Adler-Wiser formulation.[17] The static dielectric matrix is then extended to finite frequencies with a generalized plasmon pole model.[10] The full ω-dependent dielectric matrix is obtained by use of two sum rules that insure each component of ε^{-1} has the exact ω and ω^{-1} moments. This requires only the <u>ab initio</u> static dielectric matrix and the valence charge density and depends on <u>no</u> adjustable parameters.

For semiconductors and insulators, the results presented here are those obtained with the dielectric matrix evaluated within the random phase approximation (RPA). We have done calculations with exchange-correlation effects included in ε within the LDA and found that the results were altered only minimally (by < 0.1 eV). However, for the alkali metals where the electron density is low and the low $\vec{q}$ components are more dominant, the inclusion of exchange-correlation effects in the screening is shown to be quite important, and they have been included within the local density functional formalism.[16]

III. APPLICATIONS

In this section, we describe application of the theory outlined in Sec. II to several different cases and compare our results to experiment.

A. Semiconductors and Insulators

Diamond, Si, Ge, and LiCl are among the first crystals examined using the present method. These materials span a good range of band gaps, and they also allow us to examine whether the same picture for electron correlation

applies to the covalent as well as ionic solids. The quasiparticle equation, Eq. (1), is solved by expanding the quasiparticle wavefunction in terms of the LDA eigenfunctions. The underlying LDA calculations are performed using the ab initio pseudopotential method with a plane wave basis.[4] To represent adequately the local field effects which are described by the off-diagonal elements of $\varepsilon_{\vec{G}\vec{G}'}(\vec{q},\omega)$, dielectric matrices of size (depending on $\vec{q}$) 140x140 for Si and 200x200 for diamond, Ge, and LiCl are used in determining the screened Coulomb interaction. Finally, the self-energy operator in Eq. (1) must be evaluated self-consistently at the quasiparticle energy $E_{n\vec{k}}$.

Table I presents the calculated minimum gap of the four materials studied together with the experimental values.[5,6] The gaps open up dramatically as compared to the LDA values and are in excellent agreement with experiment. We find that, for a full physical description of Σ and the quasiparticle properties, three elements in the theory are crucial: proper account of the nonlocality of G; inclusion of the full dielectric matrix (local field effects) in the screening of the bare Coulomb interaction; and adequate treatment of dynamical effects in the screening.

We illustrate these points by presenting our results in four successively better approximations to Σ: the LDA, the Coulomb-hole-screened-exchange (COHSEX) approximation [1] without local fields, the COHSEX approximation with the full static dielectric matrix, and finally, the full GW approximation. The COHSEX approximation for Σ is essentially static and thus leaves out the effects of dynamical renormalization. Figure 1 summarizes the results for the minimum (indirect) gap E_g and the E_1 optical transition ($L_{3v'} \rightarrow L_{1c}$) of Si. This figure dramatically demonstrates the importance of local fields to the band gaps and illustrates the excellent results from the full

dynamical calculation. We find very similar behaviors for the other gaps and also for other materials showing that electron correlations in the different materials are described by the same physical picture. (See Table II). In particular, the opening of the band gaps with the inclusion of local field effects is understood in terms of dielectric response. Local fields describe the inhomogeneity of the electronic polarizability in the unit cell. Screening at points of high charge density (valence-state sites) is more effective than at points of low charge density (conduction-state sites) and thus deepens the Coulomb-hole contribution to the electron self-energy for states with wavefunction at regions of concentrated charge density. For insulators, this effect lowers the energies of the occupied states relative to the unoccupied states giving rise to an increased band gap.

A comparison between the experimental direct optical transition energies [5,18-21] and the calculated results is given in Table III for Ge, Si, and diamond. LiCl is not included because the optical spectra are dominated by excitonic features. As seen from the table, the theoretical results are all within 0.1-0.2 eV of the experimental numbers except for the very high energy ones in diamond where there are rather large uncertainties in experiment. This kind of agreement is a dramatic improvement over previous theories [11-14]. In fact, the present results are comparable to results from empirical methods [22] in which the band structure is obtained by fitting to optical data using several parameters.

Besides the minimum band gaps and optical transitions, the present approach yields excellent band dispersions. A comparison of the calculated Ge quasiparticle band structure with data from angle-resolved photoemission measurements [23] is given in Fig. 2. The agreement between theory and experiment is again extremely good. The theoretical results are, in general,

well within the experimental errors. Similar level of agreement with experiment has been obtained for the other three materials. Results for LiCl are presented in Table IV.[6, 24-26] A comparison with available inverse photoemission and indirect optical transition data [27-30] shows that the conduction band dispersions are also in good agreement with experiment. (See Table V.)

Although the present theory is for excited states and the LDA is strictly a theory for the ground state, it is of interest to present our results in the form of a correction to the LDA eigenvalues since the LDA values are widely used as particle excitation energies in interpreting experiments. The difference between the calculated quasiparticle energies and the LDA eigenvalues are plotted as a function of the quasiparticle energy in Fig. 3. All four materials show similar trends. The required correction is dominated by a large jump at the energy gap and has a rather smooth energy dependence away from the gap region. The discontinuous jump at the gap reflects the fact that there is a qualitative change in the character of the wavefunction between the valence and conduction band states. Also, the conduction band states show a different energy dependence than that of the valence band states. The correction is therefore not just a rigid shift. In addition, the distribution of the correction between the conduction and valence band states are materials dependent. This should have important implications to LDA based theories on heterojunction band offsets or Schottky barriers since an accurate determination of the line-up of the quasiparticle band edges is required in both cases. Our analysis also shows that the assumption usually made in applying the self-interaction correction to the LDA to solids is not correct.[31] As illustrated clearly in Fig. 3, the correction is not simply due to a lowering of the valence electron energy by removal of the spurious

self-interaction energy in the LDA. In fact, to fix the LDA band gap of the homopolar semiconductors, the correction is mostly to the conduction band energies.

B. Semiconductor Surfaces

The many-body theory for the quasiparticles is extended to the case of surfaces.[15] The aim here is to provide a theoretical framework for predicting not only the structure but the excitation spectra of a surface from first principles. Similar to the case of the bulk band gap problem, usage of LDA eigenvalues as surface state energies has yielded large underestimation of the gap between the occupied and empty surface states. The present procedure involves, first, the determination of the atomic coordinates from a density functional total energy calculation and then calculation of the quasiparticle surface state energies. This will allow well-founded comparison of theory to surface spectroscopic measurements.

Because of their geometric simplicity and availability of detailed experimental data, the prototype systems chosen for the many-body calculation are the recently examined As overlayer on the Ge(111) and Si(111) surface.[32,33] The As atoms are found to substitute for the outermost layer surface atoms of the host. The resulting surface is chemically passive and stable against reconstruction exhibiting a 1x1 surface periodicity. The extra valence electron on the As leads to fully occupied dangling bond (lone pair) surface states that have been observed by angle-resolved photoemission experiments.[32,33]

The calculations are carried out using a repeated slab geometry with 12 layers of atoms and 4 layers of vacuum region. The structural relaxation of the surface As layer and the corresponding ground-state charge density are obtained from a LDA calculation using *ab initio* pseudopotentials. Figure 4

displays the change in the total energy as a function of the displacment of the As layer from the ideally terminated Si position for the Si(111):As surface. The equilibrium relaxation is achieved when the As layer is moved outward by 0.16 Å. This is in excellent agreement with the recent experimental finding of a relaxation of 0.17 Å from X-ray standing wave measurements.[34]

After the structure is determined, the quasiparticle energies including those for the surface states are calculated using precisely the same theoretical procedures as described above. The major results are presented in Figs. 5 - 7. In Fig. 5, the LDA surface bands are plotted (dashed lines) against the projected quasiparticle band structure of Ge. In addition to the lone pair states, we note that there is also an empty surface state band in the gap which corresponds to anti-bonding back bond states. These have not been observed experimentally. In the same figure, the results for the many-body calculation of the quasiparticle surface states (solid lines) are given. Very similar results are obtained for the Si(111):As system. The primary effect on the occupied lone pair states is to lower the band relative to the valence band maximum, broaden the band, and, in the case of Ge(111) surface, correct the unusual dispersion near Γ. All three are required for better agreement with experiment. The effect on the empty surface states is more dramatic. These states are substantially shifted upwards opening the gap between empty and occupied surface states by nearly 1 eV at some k-points. The position of the empty surface staes is thus a prediction of the present theory which is verifiable by experiment. The final results for the occupied surface states are compared to the angle-resolved photoemission data in Figs. 6 and 7. For both systems, the agreement is within the estimated errors associated with experimental determination of the bulk

valence band edge (±0.1 eV) and the theoretical results (±0.1 eV).

The quasiparticle surface state results here thus address the surface state band gap problem mentioned above. This has implications for LDA calculations of surface bands on other semiconductor surfaces. The many-body approach yields a larger gap between empty and occupied surface states than that found in the LDA calculation. However, it is not possible to determine this difference based purely on considerations of the bulk calculation. A survey of the experimental data shows that the errors in the surface state E_g are, in fact, smaller than for the corresponding bulk gaps. This is related to the fact that the magnitude of the many-body corrections for states intermediate in the gap seems to depend on the degree of conduction band or valence band character of the surface state wavefunction.[15] The dangling bond surface states (in the bulk energy gap), in general, are a mixture of both conduction and valence band character. Our results for the prototype systems also show a deepening of the occupied surface state energies relative to the valence band maximum when compared to the equivalent LDA values. Finally, corrections to the dispersion of the surface state bands can, in general, be expected although they may be small in some cases. For the present cases, the self-energy corrections to the LDA for the dispersion of the surface states are about 20%.

IV. SUMMARY AND CONCLUSIONS

We have presented a first-principles theory for the quasiparticle energies and electronic excitation spectra in solids. The electron self-energy operator is evaluated to first order in the dynamically screened Coulomb interaction including local field effects. This approach is shown to yield highly accurate excited-state properties for real materials with the only basic input being the atomic number of the constituent elements.

Applications have been made to the semiconductors, ionic insulators, and alkali metals. In all cases, the theoretical results are in excellent agreement with available data from optical, photoemission, and inverse photoemission experiments although we have not discussed the alkali metal results here. The theory is also shown to extend beyond the case of the simple bulk crystals, e.g., to surfaces and chemisorption systems. It thus provides a procedure using the atomic coordinates given by total-energy calculations to predict the surface state energies.

Although the method described here is a rather recent development, we feel its successes so far are very encouraging and clearly demonstrate the viability of the present approach as a method for ab initio calculation of the quasiparticle properties of real materials. The same theoretical framework should be applicable to predict quantitatively the excited-state properties of a host of other condensed matter systems not discussed here.

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TABLE I. Comparison of calculated band gap E_g (in eV) with experiment. The results for Ge include relativistic effects.

	LDA	Present Theory	Expt.
Diamond	3.9	5.6	5.48[a]
Silicon	0.52	1.29	1.17[a]
Germanium	<0	0.75	0.744[a]
LiCl	6.0	9.1	9.4[b]

[a] Ref. 5 [b] Ref. 6

TABLE II. Trends are shown for the fundamental gap E_g of diamond, Si, Ge, and LiCl for several approximations to the electron self-energy operator as described in the text. For Ge, the indirect gap is shown including relativistic effects.

	LDA	COHSEX No LF	COHSEX LF	GW
Diamond	3.9	5.1	6.5	5.6
Si	0.52	0.50	1.70	1.29
Ge	0.07	0.33	1.09	0.75
LiCl	6.0	8.2	10.4	9.1

TABLE III. Comparison between theory and experiment for optical transitions in Ge, Si, and diamond.

	LDA	Present Work	Expt.
Ge			
$\Gamma_{7v}\rightarrow\Gamma_{8v}$	0.30	0.30	0.297[a]
$\Gamma_{8v}\rightarrow\Gamma_{7c}$	-0.07	0.71	0.887[a]
$\Gamma_{8v}\rightarrow\Gamma_{6c}$	2.34	3.04	3.006[a]
$\Gamma_{8v}\rightarrow\Gamma_{8c}$	2.56	3.26	3.206[a]
$X_{5v}\rightarrow X_{5c}$	3.76	4.45	4.501[a]
Si			
$\Gamma_{25'v}\rightarrow\Gamma_{15c}$	2.57	3.35	3.4[b]
$\Gamma_{25'v}\rightarrow\Gamma_{2'c}$	3.26	4.08	4.2[c]
$L_{3'v}\rightarrow L_{1c}$	2.72	3.54	3.45[b]
$L_{3'v}\rightarrow L_{3c}$	4.58	5.51	5.50[b]
Diamond			
$\Gamma_{25'v}\rightarrow\Gamma_{15c}$	5.5	7.5	7.3[d]
$\Gamma_{25'v}\rightarrow\Gamma_{2'c}$	13.1	14.8	15.3±.5[e]
$X_{4v}\rightarrow X_{1c}$	10.8	12.9	12.5[c]

[a]Ref. 18 [b]Ref. 19 [c]Ref. 5 [d]Ref. 20
[e]Ref. 21

TABLE IV. The results (in eV) of the present theory for LiCl are compared to experiment for gap E_g, Cl 3p bandwidth W_{3p} and the separation between the Cl 3s and 3p bands $E_{3p} - E_{3s}$.

LiCl	Present Theory	Expt.
E_g	9.1	9.4[a]
W_{3p}	3.8	4.0±0.2[b]
$E_{3p}-E_{3s}$	11.6	11.6±0.5[c] 11.0±0.6[d]

[a]Ref. 6 [b]Ref. 24 [c]Ref. 25
[d]Ref. 26

TABLE V. Comparison of calculated results to optical and inverse photoemission data (in eV).

	LDA	Present Theory	Expt.	
Silicon				
$\Gamma_{25'v}\rightarrow L_{1c}$	1.51	2.27	2.1[a]	2.4±.15[b]
$\Gamma_{25'v}\rightarrow L_{3c}$	3.37	4.24		4.15±.10[b]
Germanium				
$\Gamma_{8v}\rightarrow L_{6c}$	3.62	4.33	4.3±.2[c]	4.2±.1[d]
$\Gamma_{8v}\rightarrow L_{4,5c}$	3.72	4.43		
$\Gamma_{8v}\rightarrow L_{6c}$	7.00	7.61	7.8±.6[c]	7.8±.1[d]

[a]Ref. 27 [b]Ref. 28 [c]Ref. 29 [d]Ref. 30

FIGURE CAPTIONS

Fig. 1. Theoretical results (see text) vs. experimental values: (a) E_g and (b) the E_1 optical transition.

Fig. 2. Photoemission data from Ref. 23 vs. theoretical quasiparticle energies of Ge.

Fig. 3. Difference between calculated quasiparticles energies and LDA eigenvalues.

Fig. 4. Calculated relaxation energy vs. displacement of As overlayer.

Fig. 5. Surface state energies based on the LDA eigenvalues are compared to the quasiparticle surface state energies of Ge(111):As along symmetry directions indicated. The quasiparticle bulk projected band structure is shown.

Fig. 6. The calculated occupied quasiparticle surface state energies for Ge(111):As are compared to data from angle-resolved photoemission (Ref. 32).

Fig. 7. Same as Fig. 6 except for Si(111):As. Experimental data are from Ref. 33.

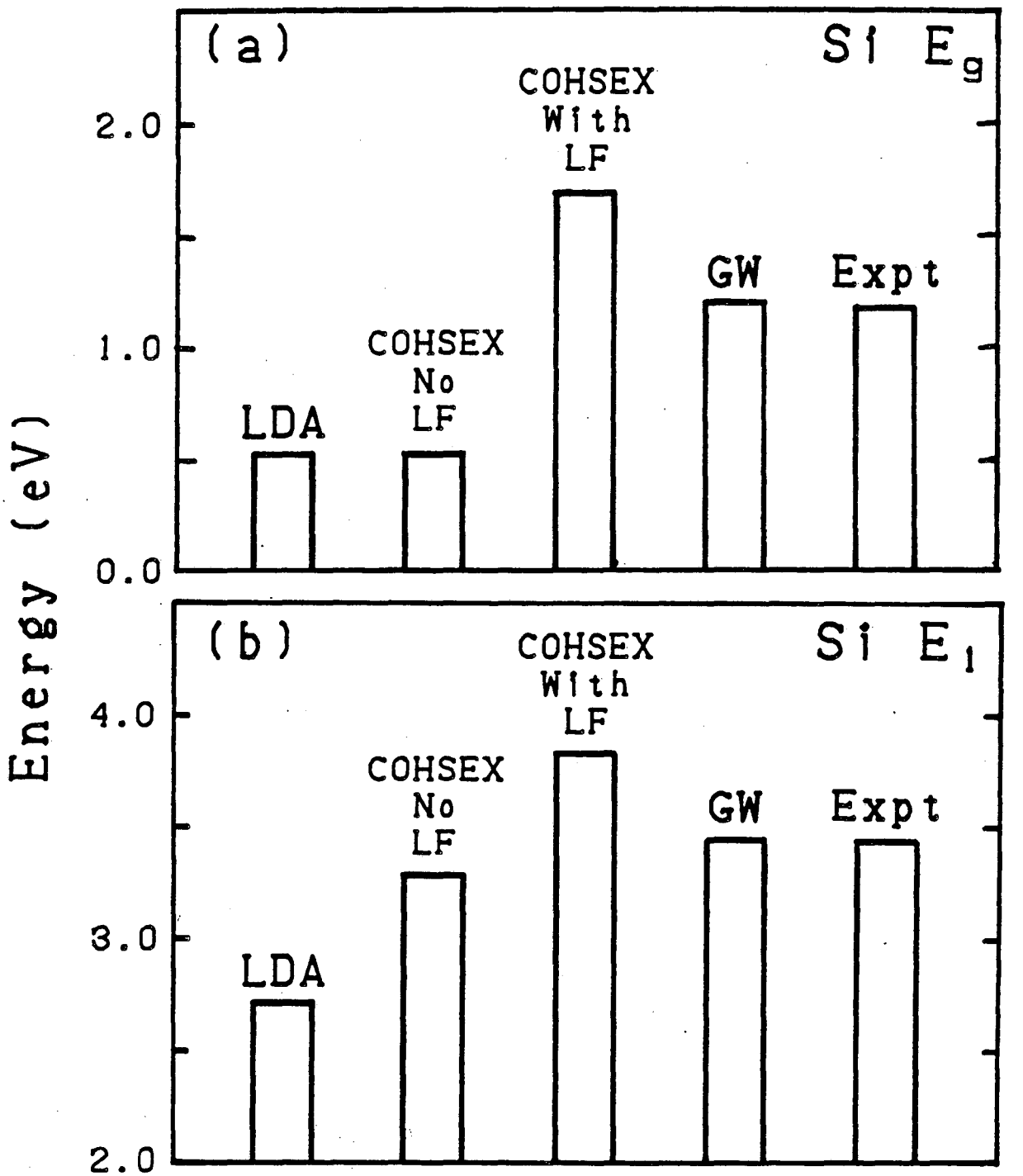
(a)
Si E_g
COHSEX
With
LF
GW
Expt
COHSEX
No
LF
LDA
2.0
1.0
0.0
Energy (eV)
(b)
Si E_1
COHSEX
With
LF
COHSEX
No
LF
GW
Expt
LDA
4.0
3.0
2.0

FIG. 1

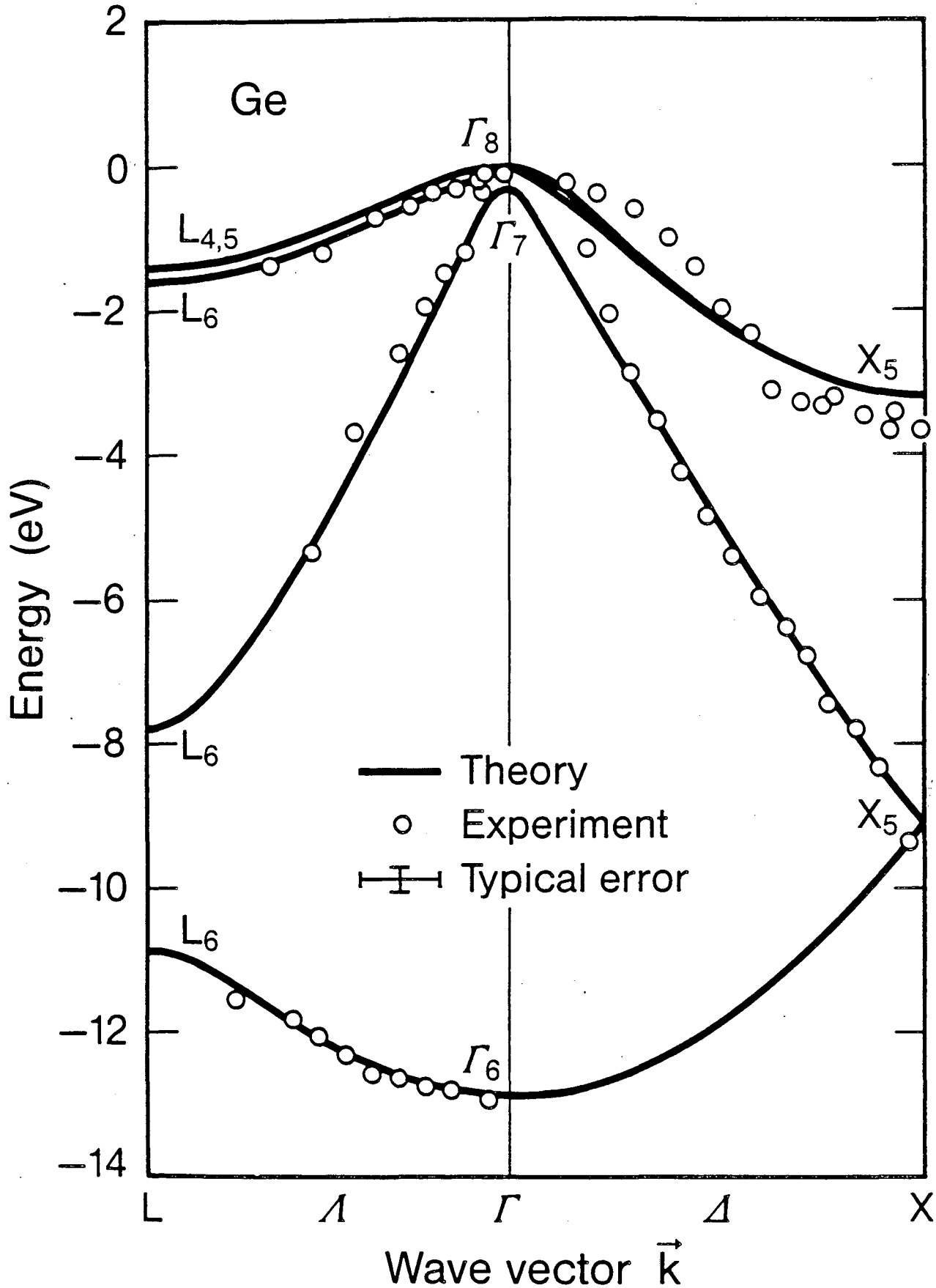
Ge
Γ8
Γ7
L4,5
L6
X5
L6
X5
L6
Γ6
Theory
Experiment
Typical error
2
0
−2
−4
−6
−8
−10
−12
−14
Energy (eV)
L
Λ
Γ
Δ
X
Wave vector k

FIG. 2

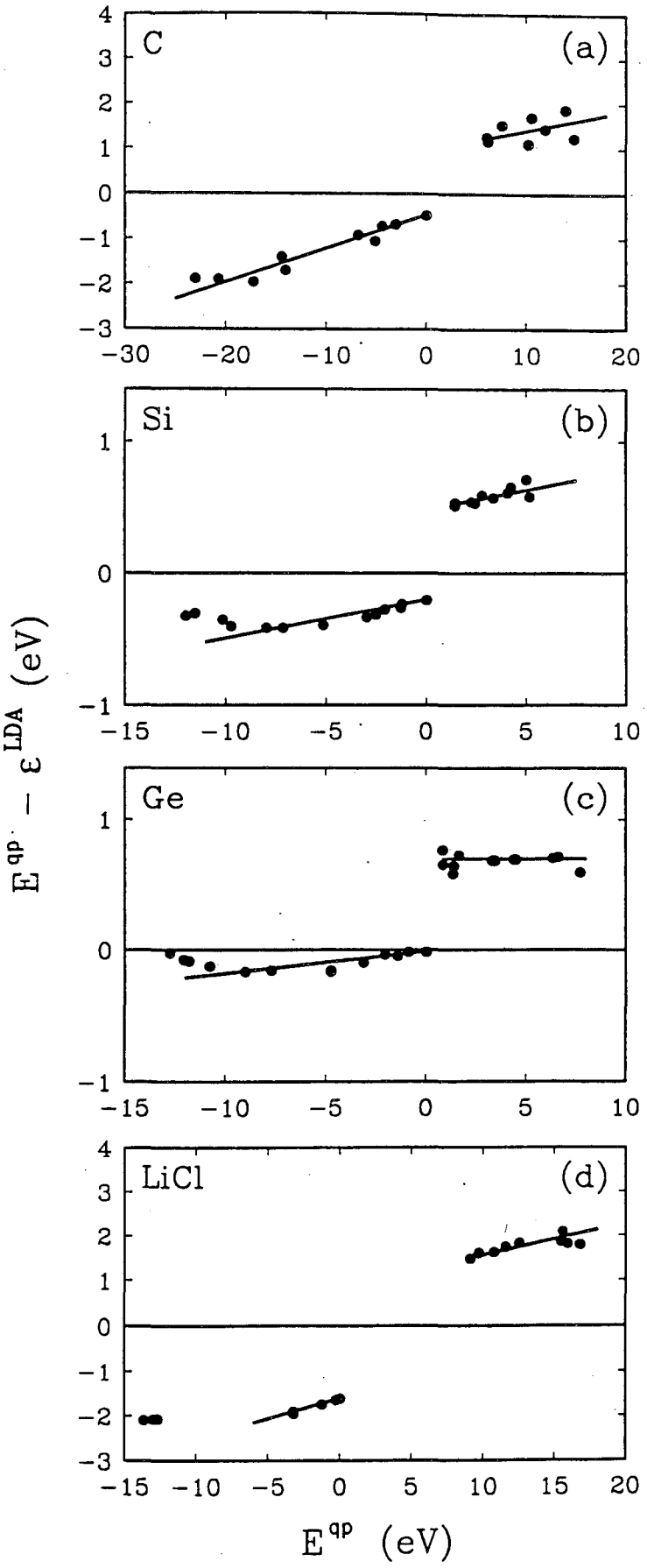

FIG. 3

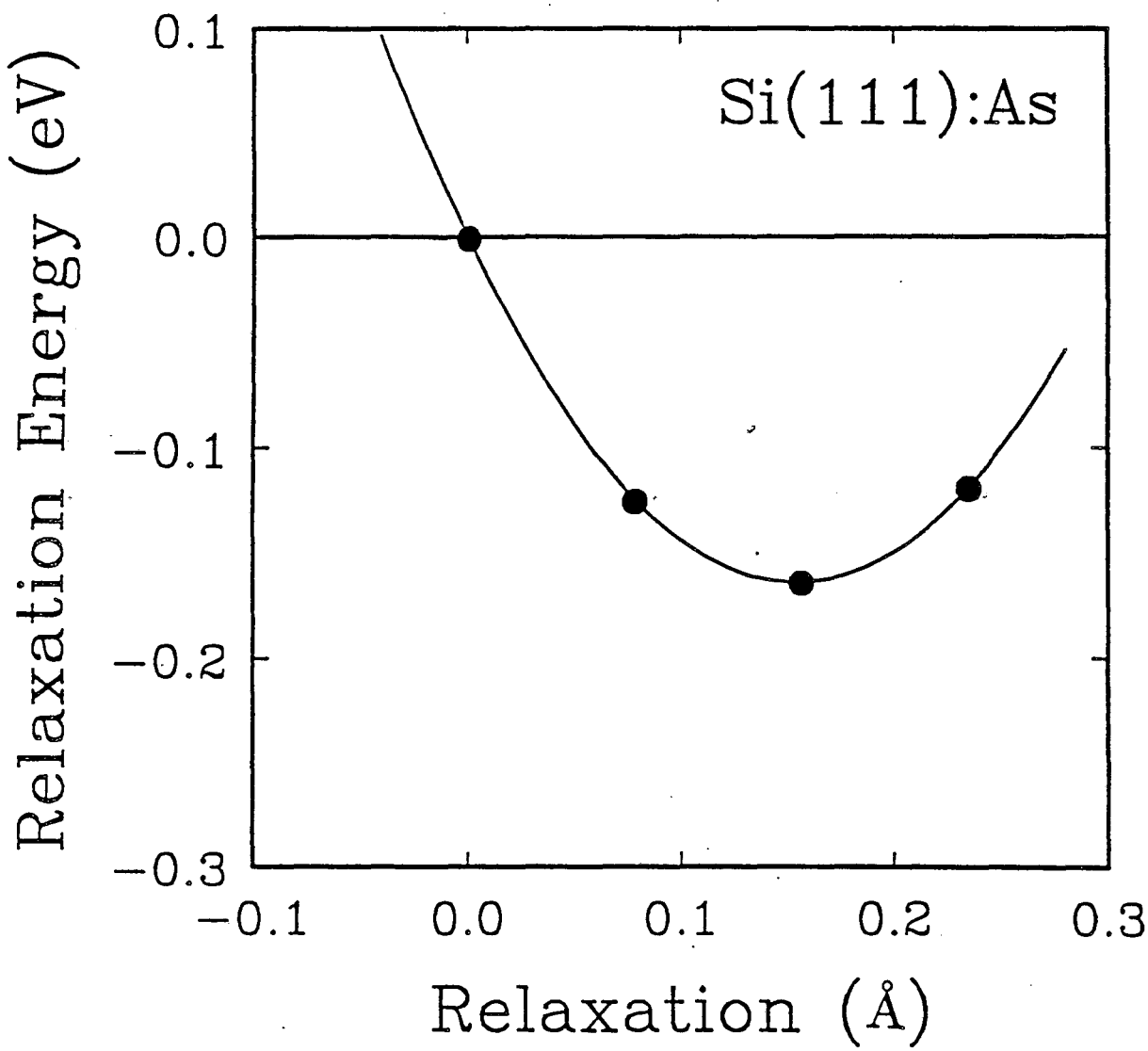
Si(111):As
Relaxation Energy (eV)
0.1
0.0
−0.1
−0.2
−0.3
−0.1
0.0
0.1
0.2
0.3
Relaxation (Å)

FIG. 4

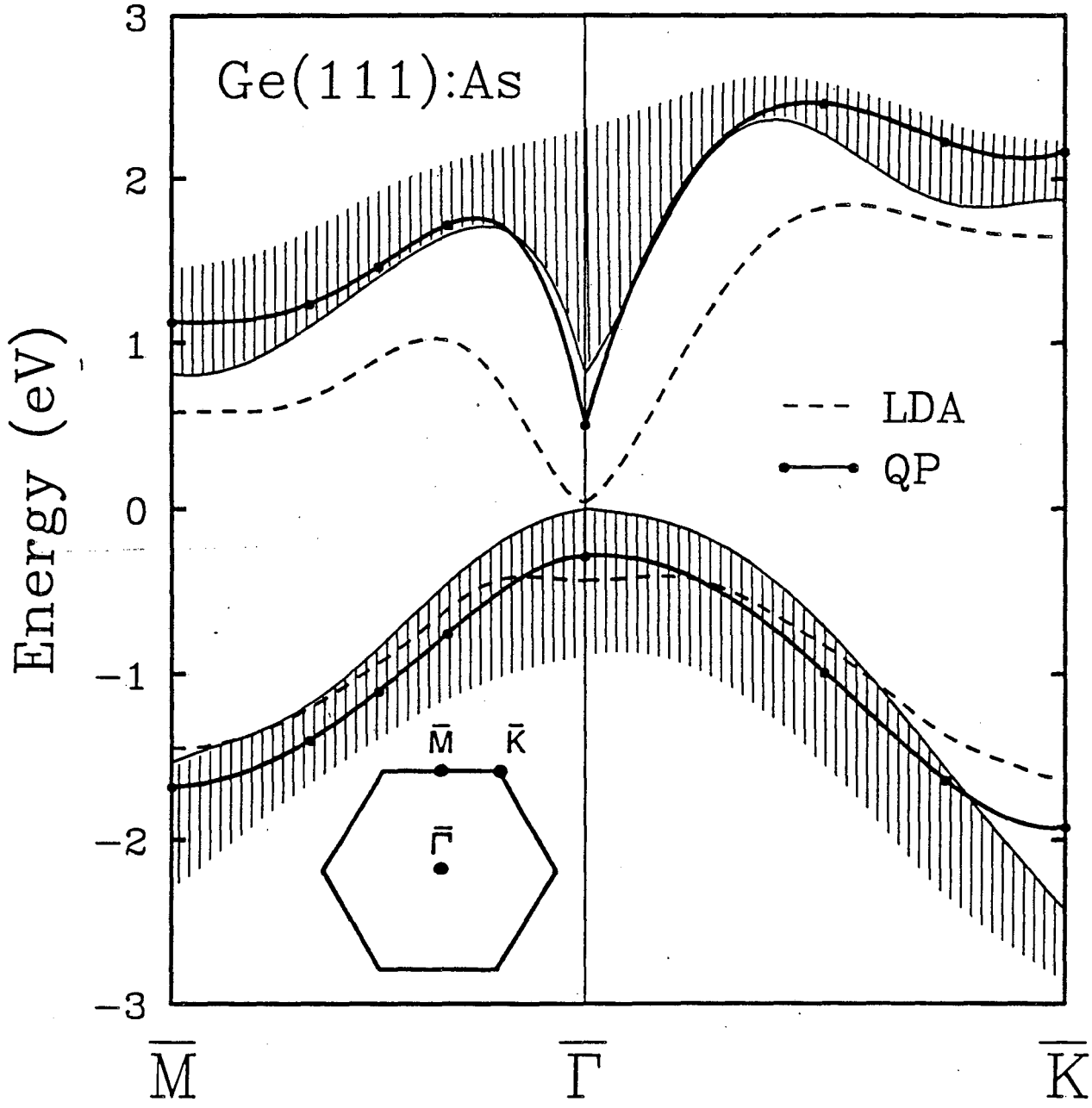

FIG. 5

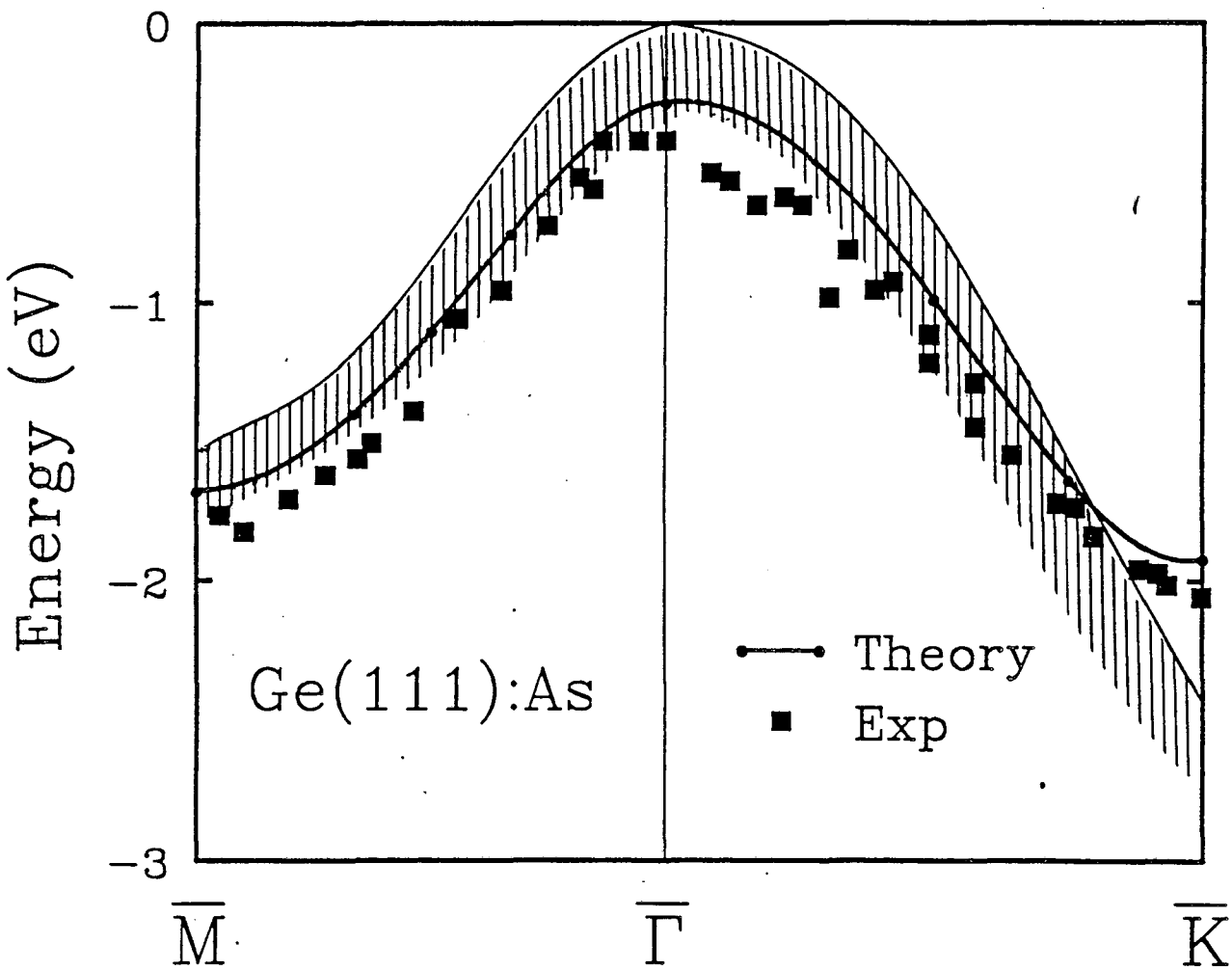

FIG. 6

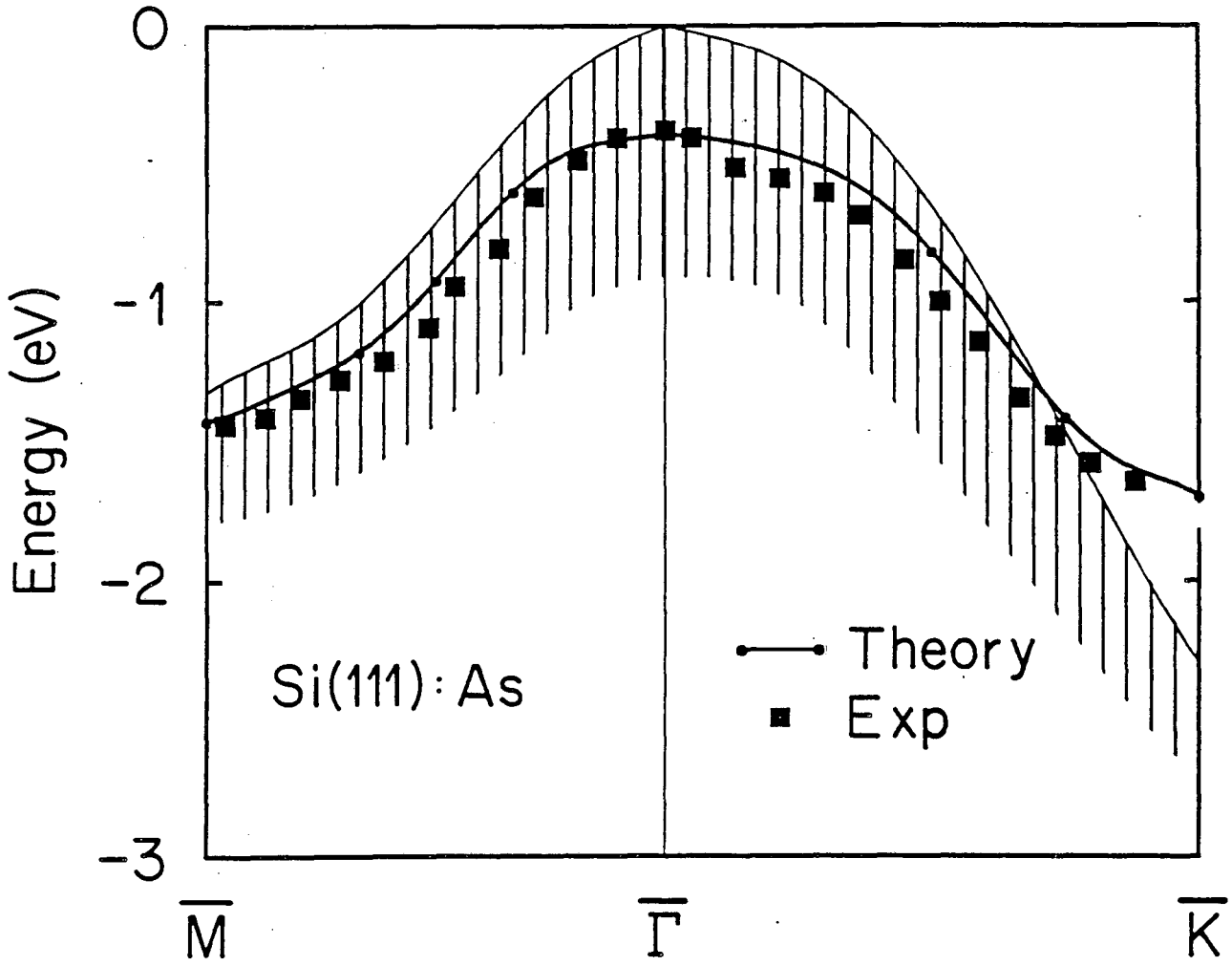

FIG. 7

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