

# Theoretical predictions of electronic materials and their properties

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In this article, I first define the basic structure of modern 'first-principles theory of real materials' (including old references), and then I review recent applications to electronic materials. I argue that electronic structure theory of real materials has advanced to the point where bold predictions of yet unmade materials and of unsuspected physical properties are being made, fostering a new type of interaction with experimentalists. I review the basic characteristics of this new style of theory, illustrating a few recent applications, and express opinions as to future challenges.

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## Abbreviations

<b>CBM</b>	conduction band minimum
<b>EMA</b>	effective mass approximation
<b>LAPW</b>	linear augmented plane wave
<b>LDA</b>	local density approximation
<b>LMTO</b>	linear muffin tin orbital
<b>VBM</b>	valence band minimum
$\Delta H^f$	formation enthalpy
$\Delta H^m$	migration enthalpy
$\Delta E_v$	valence band offset

## Introduction

### The scope and structure of first-principles theory of 'real materials'

retaining the complexity and specificity of actual solids, without losing track of the underlying global trends and basic physics.

#### What's done?

The basic structure of electronic structure theory is drawn from text-book quantum-mechanics. A 'system' (atom, molecule, solid, nanostructure) is defined via its 'external potential'  $V_{ext}(\mathbf{r})$ , which includes information on the atomic

comprising the system, plus, when appropriate, external (e.g. electric, magnetic) fields. One then sets up an effective single-particle Schroedinger equation:

$$\left\{-\frac{1}{2}\nabla^2 + V_{ext}(\mathbf{r}) + V_{screening}(\mathbf{r}, \rho)\right\}\Psi_i(\mathbf{r}) = \epsilon_i \Psi_i(\mathbf{r}) \quad (1)$$

where  $V_{screening}$  is the systems response to  $V_{ext}$ . The screening potential, depends on the density matrix  $\rho$ . Where  $\{\psi_j\}$ ,  $\{\epsilon_j\}$  are the single-particle wavefunctions and energies, respectively. Assuming at first a given geometry (hence, a given  $V_{ext}(\mathbf{r})$ ) and using a specific microscopic model of screening (e.g. the local density approximation [LDA] [1]), one solves Equation 1 iteratively, using the boundary conditions appropriate to the system at hand (e.g. periodic bulk solids, isolated quantum dots, etc.). Iterations are needed because  $V_{screening}$  depends on  $\rho$  and the latter is obtained from the wavefunctions  $\psi$  via  $\rho(\mathbf{r}, \mathbf{r}') = \sum_j \psi_j^*(\mathbf{r})\psi_j(\mathbf{r}')$ . The sequence is; one assumes  $\rho$ , then computes  $V_{screening}(\rho)$ , then solves Equation 1 to find  $\{\psi_j\}$ , then recomputes a new  $\rho$  from the latter, and continues to self-consistency. When self-consistency is attained, for a

obtains the total electron + nuclear energy [2] of that geometry:

$$E_{tot}\{R_\alpha, \alpha = 1...N\} = \sum_i \epsilon_i - \frac{1}{2}E_H - \frac{1}{4}E_{XC} + \frac{1}{2}E_{i-j} \quad (2)$$

where the first term is the sum of single particle energies,  $E_H$  is the electron-electron Coulomb (Hartree) energy,  $E_{XC}$  is the exchange-correlation energy, and  $E_{i-j}$  is the ion-ion energy. The forces on all  $N$  atoms are then obtained from  $E_{tot}$ ; one seeks the geometry that produces no forces:

$$\vec{F}_\alpha = \partial E_{tot} / \partial R_\alpha = 0 \quad (3)$$

#### What's the input and what's the output?

Given the inputs, the  $N$  atomic number  $\{Z_\alpha\}$  and initial

total energy with respect to unit cell deformations yield elastic constants  $\{C_{ij}\}$ , whereas second derivatives with respect to collective atomic displacements yield force constants, hence the phonon spectrum. Bonding information is gleaned from the charge-density.

$$\rho(\mathbf{r}) = \sum_j \psi_j^*(\mathbf{r})\psi_j(\mathbf{r})$$

Response to external perturbations (pressure, strain,

rotation for the perturbed system, or the linear response methods [3]. This yields quantities such as pressure equation of states, strain deformation potentials, and polarizabilities. When the eigenvalues  $\{\epsilon_j\}$  are interpreted

the systems energy level structure, the transition matrix

## What made it possible?

from conceptual to computational breakthroughs, as well as from progress in computer technology. The main enabling steps are as follows:

1. The formulation of  $V_{\text{screening}}$  in terms of the density  $\rho$  by Kohn and Sham [1].
2. The evaluation of the functional form of useful approximation to  $V_{\text{screening}}(\rho)$ , for example, the early exchange and correlation functional of Singwi *et al.* [4] and of Hedin and Lundqvist [5], and the most accurate one by Ceperley and Alder [6], and Perdew and Zunger [7].
3. The simplification of  $V_{\text{ext}}$  in terms of atomic pseudopotentials [8] that are calculable from well-defined (e.g. LDA) atomic models, [9–11] rather than empirically [12].
4. The formulation of nondivergent methods for evaluating  $E_{\text{tot}}$  and  $F_{\alpha}$  of infinite systems (e.g. in momentum-space) [2].
5. The development of efficient computational strategies to solve Equation 1, once general forms of  $V_{\text{ext}}$  and  $V_{\text{screening}}$  are formulated. This includes plane-wave methods (e.g. [2]), LAPW (linear augmented plane wave) [13] and LMTO (linear muffin tin orbital) [14,15].

matrix problems underlying Equation 1, for example, iterative-diagonalization, [16,17] and conjugate gradient [18].

7. The development of strategies for displacing atoms (Equation 3) simultaneously with refining charge densities [19] (Equation 1). And, more recently, the combination of the latter [19] with molecular dynamics by Car and Parrinello [20].

parallel architectures.

## The characteristics of current first-principles approaches to prediction of materials properties

From the traditional band structure models (inferred from the classic solid state text books in a number of important ways.

### The focus is on the physics

gral evaluation approximations), but focuses instead on

structure of matter.

really done in the calculation, or to suspect that one is 'getting the right answer for the wrong reason,' because there are now a number of independent approaches that systematically give the same answers. These are the LAPW and converged pseudopotential calculations (unfortunately, there are still quite a few LDA-based methods around that are poorly implemented producing unreliable results.)

### Realism is key

Text-book simplifications including one-dimensional models; spherical-potentials; nearly free-electron models; simple tight-binding and other 'elegant' and 'back of the envelope' constructs have given way to an approach that tackles the real complexity and diversity of matter, without losing sight of the underlying physics.

### The approach is reflective

Discrepancies with experiments are analyzed by searching for specific inappropriate physical inputs/assumptions, rather than by using empirical adjustments to cover-up our basic ignorance. For example, when a 'wrong' band gap was calculated early on [21] for LiF (9.8 eV, instead of the measured and previously calculated 14.2 eV) using a 'right' method (LDA with no adjustments [21]), the analysis of this shocking discrepancy led to a deeper understanding of fundamental (self-interaction) corrections [21] to the underlying formalism. Similar discrepancies led later on

to the development of quasiparticle corrections to the band structure.

### The attitude is bold and interactive

This type of theory sometimes predicts unsuspected stable structures, or materials with previously unknown properties before experiments are carried out. The time taken between the theoretical prediction and its experimental testing is often shorter than the duration of a PhD thesis.

described above characterize mostly the electronic structure theory of 'electronic materials,' that is semiconductors. Indeed, the structure–function relationships underlying semiconductority lead themselves to this type of materials more readily than, for example, superconductivity, or and dynamic correlations play a more crucial role.

## Theory predicts defect properties in III-V nitrides

Using the same formalism, Niemi and Nieminen [27] have used the pseudopotential LDA

approach to study the properties of defects in GaN. The

(via acceptors) and n-type doping (via donors). The theory gives access to five basic quantities: firstly, the lowest-energy location and geometry of the defect in the lattice; secondly, the formation enthalpy  $\Delta H_f(A^q, \epsilon_f)$  of the charge state  $q$ , as a function of the Fermi energy  $\epsilon_f$ . The lower  $\Delta H_f(A^q, \epsilon_f)$  is, the larger the equilibrium concentration of  $A^q$  (negatively-charged defects (donors) form more easily in p-type materials ( $\epsilon_f$  near the VBM), but their formation releases electrons, thus contributing to n-type behavior. Negatively-charged defects (acceptors) form more easily in n-type materials ( $\epsilon_f$  near the CBM [conduction band minimum: 'shallow donor']), but their formation

ly, the donor (0/+) [or acceptor (0/-)] transition 'energy level' required to change the charge state. If the (0/+) level is near the CBM, the system becomes n-type, whereas if

'shallow acceptor', the system becomes p-type. Deep donors or acceptors do not contribute carriers; fourthly, the migration barrier energy  $\Delta H_m(A^q, \epsilon_f)$  for diffusion of  $A^q$  (the larger it is, the less mobile is  $A^q$ ), and fifthly, the identification of the defect which will actually compensate a given

Regarding 'n-type doping' via donors, theory found the following, firstly,  $V_{\text{N}}^+$  (nitrogen vacancy) is a shallow donor, (producing upon ionization, electrons), but its formation energy  $\Delta H_f(V_{\text{N}}^+; \text{n-type})$  is too high to warrant an appreciable carrier density, so  $V_{\text{N}}^+$  is not the source of the observed n-type behavior. However, secondly,  $\text{Si}_{\text{Ga}}^+$  and  $\text{O}_{\text{N}}^+$  (Si on Ga site; oxygen on N site) are much easier to

shallow donor states. Thus, these impurities are likely to be the reason for the observed n-type behavior. Thirdly,  $\text{H}^+$  is a shallow donor, and its equilibrium lattice location

mation enthalpy permits a large equilibrium concentration in p-type samples. The migration barrier  $\Delta H_m$  is low ( $\sim 0.7$  eV), so  $\text{H}^+$  is highly mobile. It compensates  $\text{Mg}_{\text{Ga}}^-$  (see below).

Regarding 'p-type doping' via acceptors, theory found the following, firstly,  $V_{\text{Ga}}^{3-}$  (Ga vacancy) has a low formation energy, but its acceptor level is deep ( $\sim 1$  eV above VBM),

ered by attachment to  $\text{O}_{\text{N}}^-$  (forming  $V_{\text{Ga}}^-$  acceptor-donor pair). Secondly,  $\text{H}^-$  has a shallow acceptor above the VBM, but its formation enthalpy in n-type material is high (leading to limited solubility). It is almost immobile, due to a large  $\Delta H_m$ . Hence, its ability to compensate donors such as  $\text{Si}_{\text{Ga}}^+$  is limited. Thirdly,  $\text{Mg}_{\text{Ga}}^-$  and  $\text{Be}_{\text{Ga}}^-$  are shallow

enthalpies, and are thus predicted to lead to p-type behavior. However,  $\text{Mg}_{\text{Ga}}^-$  is compensated by the equally

low formation enthalpy  $\text{H}^+$  center. High temperature and donor-acceptor pair, and recover the p-type behavior.

## Opinion

ence, show by and large a significant internal agreement, and have greatly contributed to interaction with experimental chemists. Experimenting seems to take the way by coming up first with practical dopants in GaN.

## Theory predicts the band offsets between semiconductors

When two semiconductors AC and BC form an AC/BC

$\Delta E_v(\text{AC/BC}) = E_v(\text{AC}) - E_v(\text{BC})$ . The magnitude of the offset is an important device characteristic, as it determines the ability of electrons (in the conduction band) and

junction to the other. In the past few years, first-principles electronic structure theory has been applied to predict valence band and conduction band offsets between various materials either assuming an unstrained interface (leading to a 'natural band offset') or assuming a hetero-

trial calculations, and an-electron LAPW calculations produce quite similar predictions, whereas the LMTO method sometimes gives somewhat different values. Let me first illustrate the situation, as well as the extent of agreement/disagreement with experiment by considering nitrides. LAPW calculations [28\*] give for the 'natural' offset  $\Delta E_v(\text{InN/GaN}) = 0.26$  eV, whereas the pseudopotential values is 0.3 [29]. The LMTO value [30] is 0.51 eV.

experimental values is generally excellent, often within 0.1 eV or so. This is the case for II-Vs [31] and most III-Vs [32]. Even in 'complicated' cases, where one calculates

ternary alloy ( $\text{Ga}_x\text{In}_{1-x}\text{P}$ ) that can have different degrees  $\eta$  of long range order, the agreement with experiment [34] is excellent. (In fact, the agreement with more recently measured values is even better than with the older values. The calculated value did not change.)

I would like to draw attention to three cases where the agreement between theory and the currently available

on these cases, it is essential that the conflict be resolved. Firstly, the measured [35\*]  $\Delta E_v(\text{GaN/InN}) = 1.05$  eV is considerably different from all first-principles values (0.26, [28\*] 0.3, [29] 0.5 [30]). Secondly, the currently measured value for  $\Delta E_v(\text{InAs/GaAs})$  strained on an InAs substrate is  $-0.57$  eV [with  $E_v(\text{InAs})$  below  $E_v(\text{GaAs})$ ] whereas LAPW

is  $-0.04 E_v(\text{InAs})$  being below  $E_v(\text{GaAs})$  whereas the LAPW value is  $+0.38$  eV [ $E_v(\text{InAs})$  being above  $E_v(\text{GaAs})$ ].

Thirdly, indirect experimental evidence discussed in [32] (see also F. (I. CL) 0.84, V. L. F. (I. A.) 1.0) and the theory [32] produces a reverse order of band edges.

### Opinion

The three discrepancies between theory and experiment for GaN/mn, GaAs/mnAs and InSb/mnSb are much larger than the stated theoretical error bars, so the experimental determination (e.g. the degree of interfacial coherence maintained in the sample, and the accuracy of determination of the valence band edge) needs to be re-examined.

### Spectroscopy of quantum dots explained

Semiconductor ‘quantum dots’ with typical dimensions of 20–100 Å can be synthesized as free-standing objects, or as semiconductor-embedded objects. Free-standing dots (e.g. InP, CdSe) are grown by colloidal methods, are strain-free, nearly spherical and have chemically passivated sur-

faces. Colloidal quantum dots, grown by molecular beam epitaxy, are highly (but coherently) strained and have pyramidal or dome shapes. Progress made in the growth of ‘free-standing’ quantum dots and in the growth of semiconductor-embedded (‘self-assembled’) dots has opened the door to new and exciting spectroscopic studies of quantum structures. These have

revealed a rich variety of phenomena, including the red shift, exchange-splitting, strain-induced splitting, and Coulomb blockade transitions. These new observations

have created the need for developing appropriate theoretical tools capable of analyzing the electronic structure of  $10^3$ – $10^6$  atom objects. The main challenge is to understand firstly, the way the one-electron levels of the dot

are affected by strain, surface effects, and secondly, the nature of many particle interactions such as electron–hole exchange (underlying the ‘red shift’), electron–hole Coulomb effects (underlying excitonic transitions), and electron–electron Coulomb effects (underlying Coulomb blockade effects).

In response to the challenges posed by these developments, a few theoretical models of the electronic structure of quantum dots were recently advanced. They are all based on the k-p method (see [37]), in which the wavefunction of the dot is expanded in terms of  $N_{\Gamma}$  bands of the periodic bulk material. The method range from the effective mass

approach of Norris and Bawendi [38] and Norris, *et al.* [39] and to  $N_{\Gamma} = 8$  of Jiang and Singh [40].

Most impressively, in their application to free-standing CdSe dots, Norris and Bawendi [38], succeeded in explaining, via the  $6 \times 6$  k-p method, the origin of as many as eight observed excitonic transitions in various size dots,

whereas the exchange interaction (see [41]) and the strain (see [42]) have explained the origin of the two main

excitonic transitions in CdSe and CdTe. In addition to explaining such ‘one-electron properties,’ an extended theory was recently able to explain the Stokes shift between absorption and emission as being due to electron–hole exchange interactions [42] (excitation can create either antiparallel, or parallel spins of the excited electron and the particle left behind. The splitting between these ‘singlet’ and ‘triplet’ configuration is due to exchange interactions, and is found to be dramatically enhanced in dots relative to bulk solids). An impressive success of theory in this regard is the identification of enhanced exchange interaction (as opposed to surface trapping) as the origin of the observed red shift.

In general, however, the exchange interaction contains a

long-range (LR) component which decays as a power law. Conventional wisdom [42] suggests that the LR exchange interaction in quantum dots originates, as in bulk semiconductors, from dipole–dipole coupling of the transition density between unit cells. Under this assumption, the LR contribution to the exchange interaction is

approximated by the e-h exchange in bulk semiconductors

whereas the LR contribution is set to zero. This approach fits well the observed red shift in CdSe nanocrystals. However, in the case of spherical zinc-blend quantum dots, the predicted  $1/R^3$  scaling of the red shift with size is not observed in either InP [43] or InAs nanocrystals. In both cases, the observed scaling is  $R^{-2}$ .

### Opinion

The currently used ‘theoretical technology’ for understanding the electronic structure of quantum dots is based on the traditional k-p envelope-function approach with a limited basis of  $N_{\Gamma} < 8$  bands. Despite spectacular successes, it is unlikely that the details of the electronic structure of quantum-dot systems which lack periodicity in all three dimensions and exhibit surface effects as well as interfacial strain would be adequately described using a small number of 3D-periodic  $\Gamma$ -like bulk orbitals. This approach will ultimately be limited by the number of non- $\Gamma$ -like dot states needed at the surfaces of the dots, non- $\Gamma$ -like dot states

and the exchange interaction. However, the global features of quantum confinement for sufficiently large dots will continue to be described very well by such approaches.

### Conclusions

Electronic structure theory of real materials has reached

with methodological issues, but is actively engaged in explaining a wide range of materials properties, predicting unsuspected structures, and even challenging experimental data for correctness of assignment or interpretation.

tations), the current attitude promises to signal the beginning of a new friendship between experiment and theory.

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