

## Density Functional Theory Revisited: The Mathematical and Physical Conditions for the Physical Content of the Eigenvalues

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**Abstract:** Following an introduction, we briefly recall the derivation of density functional theory (DFT) and of its local density approximation (LDA). It follows from this derivation that eigenvalues resulting from self consistent DFT calculations utilizing a single input basis set do not necessarily have much physical content. *We present necessary conditions for their greatest physical content.* We subsequently note new results from self consistent DFT calculations that agree very well with corresponding experimental ones. The latter calculations utilized the Bagayoko, Zhao, and Williams (BZW) method as enhanced by Ekuma and Franklin (BZW-EF). We show that the excellent agreement is due to the inherent and accurate physical content of results from self consistent BZW-EF calculations that strictly adhere to intrinsic requirements (conditions) germane to DFT. We describe the mathematical artifact that affects unoccupied energies when basis sets much larger than the DFT-optimal one are utilized to study materials with energy or band gaps.

**Keywords:** DFT foundation, band gap, BZW-EF method, predictive capability

### 1. Introduction

In 1964, Hohenberg and Kohn introduced density functional theory (DFT) [1] whose local density approximation (LDA) [2] was constructed by Kohn and Sham in 1965. Despite the wide spread utilization of DFT for the theoretical studies of semiconductors and insulators, among other materials, the literature reports shortfalls that seriously limit the usefulness of DFT for a highly accurate description of electronic and related properties of materials, in general, and for ab-initio prediction of these properties and of novel materials, in particular. As the dissertation advisor [3] and grand-advisor [4] of Bagayoko told him multiple times: “*With accurate electronic energies and related wave functions, it is possible to compute most properties of materials.*” The critical importance of obtaining accurate energies and related wave functions stems from the verified content of this quote.

Hence, the above reported shortfalls or limitations of DFT and LDA should be resolved. Before making any attempt in that direction, we should note the tremendously numerous reports of limitations of DFT and LDA, particularly in Physical Review B, emanate from calculations that did not search for and verifiably obtain the

minima of the occupied energies. In general, the differences between LDA calculated band gaps and corresponding, measured ones, are explained in terms of self interaction errors, for atoms and localized states in solids, derivative discontinuities of the exchange correlation energy, and missing non-local effects. *A leap of faith has been made in the literature: It consists of ascribing differences between single basis set calculation results and corresponding experimental ones to intrinsic features (or shortfalls) of DFT and LDA, even though the disagreement between several, calculated results should have hinted otherwise.*

The above situation is further compounded by the growing number of schemes, including very sophisticated ones, aimed at resolving the perceived limitations of DFT and LDA. Indeed, most of these new approaches entail adjustable parameters that change with the material under study. Consequently, the community seems to be drifting away from the search for ab-initio or first principle remedies to the reported limitations. Such remedies will usher in an era not just of highly accurate calculations of properties of materials, but also of theoretical capabilities to predict these properties and novel materials. We recall below the derivation of DFT and LDA as it sheds light on likely sources of disagreement between single basis set computational results and experimental ones without invoking any limitations of DFT or LDA.

## 2. Essentials of the Derivation of DFT and LDA

**The Hohenberg-Kohn Theorem.** The Hohenberg-Kohn theorem states that the external potential to which a collection of electrons is subjected is a unique functional of the electron density, except for a possible, additive constant to that potential. Considering an electron system subject to an external potential, the theorem means that unless two external potentials are different only by a constant, they cannot individually lead to the same electron density for the system under study. The Hamiltonian comprises kinetic, electron-electron interaction, and the applicable, external potential terms. The first two terms are known to be universal functional of the electron density. Hence, the Hohenberg-Kohn theorem means that the entire Hamiltonian that determines ground state properties of the electron system, including its ground state energy, is a unique functional of the electron density.

**The Variational Principle of DFT.** This variational principle simply states that, for a given system of electrons of density  $n$ , the energy functional  $E[n] = H[n] = T[n] + V[n] + U[n]$ , where  $T$ ,  $V$ , and  $U$  stand for the kinetic, the external potential, and the electron-electron interaction contributions to the energy, respectively, is an upper bound to the true ground state energy  $E_0[n_0]$  whenever the density  $n$  is constructed using a guessed many particle wave function that otherwise satisfies applicable constraints. For  $n = n_0$ ,  $E[n] = E_0[n_0]$ . It is particularly pertinent for us to quote from Hohenberg and Kohn [1]:

*“It is well known that for a system of  $N$  particles, the energy functional of  $\Psi'$*   
 $E_v[\Psi'] = (\Psi', V\Psi') + (\Psi', (T+U)\Psi')$  *has a minimum at the ‘correct’ ground state  $\Psi'$ , relative to*  
*arbitrary variations of  $\Psi'$  in which the total number of particles is kept constant.”*

The above variational principle clearly shows that single basis set calculations should not be expected to lead to the ground state properties if and when one employs density functional theory (DFT).

### 3. Density Functional Theory Revisited: Two Necessary Conditions for Greatest Physical Content

It is clear from the above principle that the physical content of DFT or LDA results can be very limited if the above variational principle is not heeded. *A single trial basis set calculation, however self consistent it may be, cannot verifiably reach the minima of the occupied energies and of  $E_v(\Psi')$ , that is  $E(\Psi')$ .* Further, when one performs calculations with several basis sets, if they are not such that each basis set is embedded in the one following it, up to the optimal one [5] that yields the minima of the occupied energies and of  $E_v[\Psi']$ , as identified by the fact that no larger basis set that contains it leads to any lower, occupied eigenvalues or lower  $E_v[\Psi']$ , one should not expect to have the full DFT description of the ground state of the system. *This embedding of basis sets, beginning with the smallest one, that should be no smaller than the minimum basis set accounting for all the electrons in the system under study, is a necessary condition for DFT calculations expected to lead to the ground state of an electron system in a verifiable fashion.* After all, there is an infinite number of possible  $\Psi'$ .

**The Second Necessary Condition – for Systems with Energy or Band Gaps.** The Rayleigh theorem states that when the same eigenvalue equation is solved with two basis sets of dimension  $N$  and  $(N+1)$ , such that the  $N$  functions of the first basis set are entirely included in the second of size  $(N+1)$ , then the ordered eigenvalues, from the lowest to the highest, satisfy the relation  $E_i^{(N)} \leq E_i^{(N+1)}$  for  $i \leq N$ . Upon an increase of the basis set, the charge density, the potential and the Hamiltonian change and so do the occupied energies and the energy functional  $E_v[\Psi']$ . The latter two are generally lowered. The application of the Rayleigh theorem becomes necessary when two successive calculations lead to the same occupied energies and low, unoccupied energies (generally up to +10 eV). For basis sets much larger than the optimal one, the above Rayleigh theorem leads to a continuing lowering of some unoccupied energies while the physics of the problem (H: occupied energies, etc.) is not affected. This mathematical artifact naturally translates itself into a decrease of energy gaps for discrete systems and band gaps for semiconductors and insulators. The decrease of calculated electron effective masses is due the lowering of conduction band minima.

### 4. Excellent Agreement between Recent DFT/LDA BZW-EF Results and Experimental Ones

The Bagayoko, Zhao, and Williams method, as enhanced by Ekuma and Franklin (BZW-EF), strictly adheres to the mathematical and physical conditions that guarantee the greatest, physical content for the results from DFT and LDA calculations. The initial BZW method made predictions that have been confirmed by experiment [6].

The reader is urged to consult the works of Franklin et al. [5] and Ekuma et al. [6] for a comprehensive description of the BZW-EF method. As explained in these sources, the EF enhancement consists of not necessarily following the s, p, d, and f order in adding orbitals to the basis set. It rests on the counter-intuitive fact that polarization has primacy over spherical symmetry – as far as valence electrons are concerned. Some cases of minor underestimations of band gaps by the BZW method, up to 0.3 eV, have been removed in BZW-EF calculations. Illustrative, recent results, in excellent agreement with experiment, are in the table below.

| Materials          | LDA/GGA BZW-EF Band Gaps in eV | Experiment           | Materials   | LDA/GGA BZW-EF Band Gaps in eV  | Experiment                  |
|--------------------|--------------------------------|----------------------|---|---|-----------------------------|
| w-ZnO <sup>5</sup> | 3.40 eV (at $\Gamma$ )         | 3.44 eV              | Ge <sup>6</sup><br>(Diamond structure)                | 0.65 eV ( $\Gamma$ to L)<br>GGA <sup>7</sup> 0.64 eV ( $\Gamma$ to L) LDA | 0.66-0.70 eV ( $\Gamma$ -L) |
| zb-AlP             | 2.56 eV ( $\Gamma$ to X)       | 2.45 eV $\Gamma$ -X  | zb-GaP  | 2.14 eV ( $\Gamma$ to X)  | 2.26 eV ( $\Gamma$ -X)      |
| zb-ZnS             | 3.725 eV (at $\Gamma$ )        | 3.723 eV at $\Gamma$ | zb-Li <sub>2</sub> S                                  | 3.538 eV ( $\Gamma$ -X)   | 3.542 eV ( $\Gamma$ -X)     |
| w-GaN              | 3.292= 3.3 eV (at $\Gamma$ )   | 3.4 eV at $\Gamma$   | w and zb stand for wurtzite and zinc blend structures |   |                             |

## 5. Conclusion

Results from density functional theory (DFT), including its ab-initio realizations as in the generalized gradient approximation (GGA) [7] and the local density approximation (LDA), have their greatest physical content when the pertinent calculations adhere strictly to the mathematical and physical conditions inherent to its derivation. *Self consistent DFT BZW-EF calculations accurately describe and correctly predict properties of materials.*

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