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Validity of the Slater-Janak transition-state model within the LDA+U approach

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Known with the name of the Slater-Janak transition-state model, Janak's theorem allows a calculation of charge transition levels by analyzing the Kohn-Sham eigenvalues of the density-functional theory without the need of explicitly comparing differently charged systems. Unfortunately, the usual local-density approximation (LDA) and its gradient extensions fail in describing the Kohn-Sham eigenvalues sufficiently well. In this work we show that the Slater-Janak transition state becomes a powerful tool if applied self-consistently within an LDA+U approach. We first explain this fact analytically and then present a numerical validation, calculating the Slater-Janak transition state for a selection of representative examples in GaN. The formalism is found to be valid for all the investigated examples, which are, besides oxygen donors (O_N) and carbon acceptors (C_N), also systems with negative-U effect (nitrogen vacancies, V_N) and strongly correlated electrons (europium substitutionals, Eu_{Ga}).

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I. INTRODUCTION

The electronic structure in the band-gap region of a semiconductor determines its optical and electronic nature. Intrinsic defects or impurities can induce localized states in the gap giving rise to different charge states of the system with different electronic properties. Charge transition levels are the thermodynamic quantities representing the position of the Fermi level at which a defect changes its charge state and, thus, play a crucial role in materials science.

From the theoretical point of view, however, their calculation is a demanding task. The most frequently used method to calculate them in a straightforward way is the so-called ΔSCF approach that requires a direct comparison of the total energy of different charge states of a given system. Unfortunately, using periodic boundary conditions in this approach leads to some uncertainties due to the spurious Coulomb interaction of the periodic images of the charged supercells. Several corrections have been proposed and applied in the literature.[1–3] However, their benefit in the general case is still in discussion.

The so-called Janak transition state[4] provides an alternative to calculate charge transition levels within density-functional theory (DFT). Besides a sufficiently reliable prediction of the energetical position with respect to the band edges, it requires a linear dependence of the Kohn-Sham (KS) eigenvalues on their occupation numbers. Both assumptions are not automatically fulfilled for all systems if using usual local-density approximation (LDA) of DFT. From a fundamental point of view, the eigenvalues of Kohn-Sham theory do not generally have a physical meaning. Only if the exchange-correlation potential can be described exactly, then the eigenvalue of the highest occupied state is equal to the electron chemical potential.[5] In LDA this requirement is not fulfilled, ending up, e.g., with underestimated band gaps inducing some uncertainties to the eigenvalues. The second requirement, the linearity with respect to the occupation numbers, has been recently investigated within the DFT approach by Göransson *et al.*[6] for 24 different (random) metallic alloy systems, finding that, in first approximation, the Kohn-Sham eigenvalues show a linear behavior as a function of their occupation number. However, serious deviations from this linear behavior should be expected for systems with strongly correlated electrons.

For this kind of systems, the LDA+U approach[7] is well known to improve the description of the total energy of a system of N electrons with respect to the total number of electrons and thus with respect to the occupation numbers. In this way it is ensured per construction that the ground-state total energy $E(N)$ of a system of N electrons is linear between N and $N+1$. In this work we show that such a linear behavior of the total energy also guarantees the linearity of the Kohn-Sham one-particle levels with respect to the occupation numbers and, thus, the applicability of the Janak formalism. Afterward, this is also numerically demonstrated by calculating the charge transitions for a selection of known defects in GaN (Eu_{Ga}, V_N, O_N, and C_N) via Janak's transition state. Since these comprehensive calculations are very time consuming we choose a rather approximate but efficient tight-binding method to perform the LDA+U total-energy calculations, the density-functional-based tight-binding (DFTB) framework,[8] which includes orbital-dependent potentials.[9,10] In the past, the LDA version of the method has been successfully applied to semiconductor compounds such as SiC,[11] GaAs,[12] and also GaN.[13] In addition to its efficiency the method allows for an empirical correction of the in LDA underestimated gap to its experimental value (see also Sec. III A). In this sense the choice of a tight-binding allows us to discuss the effect of the linearity of the eigenvalues separately.

The charge state transition calculated with the Slater-Janak (SJ) model is in good agreement with previous calculations for the investigated systems, demonstrating the validity of the Janak model. This work is organized as follows. In Sec. II we review the Janak transition-state formalism and discuss its application within the LDA+U formalism. In Sec. III the results of the simulation of our reference system are then presented and discussed. Finally in Sec. IV the whole work is summarized.

II. THEORY

According to Janak's theorem the Kohn-Sham eigenvalues of the DFT can be calculated as the derivative of the total energy with respect to the occupation number of the related Kohn-Sham orbital,[4]

$$\frac{\partial E[N]}{\partial \eta_i} = \varepsilon_i. \tag{1}$$

Here E is the DFT total energy, ε_i is the Kohn-Sham eigenvalue of the ith orbital, and η_i its occupation number $(0<\eta_i<1)$ so that the total number of electrons becomes $N=\Sigma_i \eta_i$. By integrating Eq. (1) it becomes possible to calculate the change in the total energy when we introduce one electron in the lowest unoccupied level of a system with N electrons that of course for the system with $N+\eta$ electrons becomes the highest occupied orbital (ε_H),

$$E^{N+1} - E^{N} = \int_0^1 \varepsilon_H(\eta) d\eta. \tag{2}$$

Assuming that the Kohn-Sham eigenvalue ε_H is a linear function of the occupation number, we obtain

$$(N/N+1) = E^{N+1} - E^{N} = \varepsilon_H\left(\frac{1}{2}\right), \tag{3}$$

which defines the SJ transition state. If we want the SJ transition state to be rigorously taken into account, $\varepsilon_H(\frac{1}{2})$ has to be calculated in a self-consistent calculation with a $\frac{1}{2}$ occupation of the highest occupied orbital that is affected by the charge transition.

However, making again use of an assumed linearity of ε_H one can also write

$$\varepsilon_H\left(\frac{1}{2}\right) \approx \frac{1}{2}[\varepsilon_H^{N+1}(0) + \varepsilon_H^{N+1}(1)] = \frac{1}{2}[\varepsilon_L^{N}(0) + \varepsilon_H^{N+1}(1)]. \tag{4}$$

In other words, a good estimate for $\varepsilon_H(\frac{1}{2})$ is obtained by averaging the eigenvalues of the lowest unoccupied orbital in the N-electron system and the highest occupied orbital in the system containing $N+1$ electrons. In the work of Göransson *et al.*[6] can be found a thorough investigation of the validity of Eq. (4) using LDA for selected examples. It gives a very good estimate of the position of the transition level as long as the Franck-Condon shift, which is due to the lattice relaxation as consequence of the charge change in the defect, is negligible. In this work we show that Eq. (3) (i.e., the self-consistent calculation of the SJ transition) is in principle able to overcome this restriction. However, a further problem of the approach remains in the correct description of ε_i for the general case. It is well known that in LDA the highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO-LUMO) gap between occupied and unoccupied orbitals is not well described, inducing in critical cases also some uncertainties into the energetic position of the KS levels. In addition, the assumption of the linearity of ε_i is not ensured for strongly localized electrons. We show that the latter problem can be coped by the use of orbital-dependent functionals beyond LDA, e.g., by a LDA+U approach.

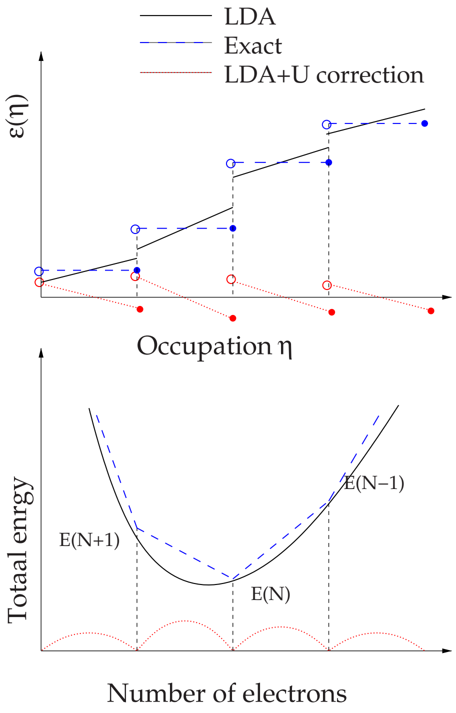

FIG. 1. (Color online) Lower part: The exact total-energy profile of a system of N electrons as a piecewise linear curve, never provided in actual DFT implementations such as LDA/GGA (solid line), where a spurious curvature is a consequence of the incorrect treatment of the self-interaction. The bottom curve is the difference between the other two (see also Ref. 15). Upper part: The LDA/GGA eigenvalue depend roughly linearly on the occupation numbers. The LDA+U corrections (dotted) are also a linear function of the occupation number. The resulting LDA+U eigenvalues are in the best case (for the ideal U value) piecewise constant.

The exact total energy $E[N]$ of a system of N electrons is a piecewise linear function of the total number of the electrons. As stated by Eschrig[14] and Cococcioni and de Gironcoli,[15] this linearity is never provided in actual realizations of the theory [DFT-LDA or DFT–generalized gradient approximation (GGA)]. In LDA or GGA the incorrect treatment of the partially occupied Kohn-Sham orbitals gives a nonlinear contribution to the total energy, resulting in an unphysical curvature of $E[N]$, as reported in Fig. 1. The linearity is hardly verified for strongly correlated electrons like those in the strongly localized d or f shells of transition metals and rare earths. Here, the application of the +U potentials largely recovers the piecewise linear behavior of the exact ground-state energy as a function of the occupations.[15] Within an LDA+U approach also the slope of the KS eigenvalues can be improved considerably. This guarantees that the assumption behind the Janak transition-state model, i.e., that the eigenvalues are linear functions of the occupation number, is automatically verified, even in the case of solids, where fractional occupations of the orbitals could occur as a consequence of the hybridization between atomiclike orbitals and environment.

If the total-energy functional $E[N]$ is, as it should be, a linear function of the total number of electrons N, then the one-particle energies are not only linear in the occupation numbers η_i but also piecewise constant (with jumps at integer values of N, see Fig. 1),

$$\varepsilon_i = \frac{\partial E[N]}{\partial \eta_i} = \frac{\partial N}{\partial \eta_i}\frac{\partial E[N]}{\partial N} = \frac{\partial E[N]}{\partial N} = \text{const.} \tag{5}$$

In other words, if we would have an ideal U, i.e., a value which perfectly recovers the piecewise linearity of $E[N]$, then the Kohn-Sham levels, defined as the first derivative of this functional with respect to the occupation numbers, would be *piecewise constant* and independent from the occupation numbers itself. The independence of the KS orbitals from their occupation numbers is for sure verified (also in DFT-LDA) in the case of extended orbitals, corresponding to the vanishing U for delocalized electrons (e.g., the band structure of an ideal solid does in fact not change adding or subtracting electrons). In the case of localized states the situation is of course different: an additional charge in the orbital will cause a change in the form (wave function) of the orbital.

In the following we present a short overview of the LDA+U approach. We restrict ourselves to the spin-unpolarized case; the spin-polarized extension of the formalism can be found elsewhere.[10] The LDA+U correction to the total energy is

$$E = E_{\text{LDA}} - \sum_{\mathcal{M}} \left[\frac{1}{2}\overline{U_{\mathcal{M}}} N_{\mathcal{M}}(N_{\mathcal{M}} - 1) - \frac{1}{2}\sum_{i \neq j \in \mathcal{M}} U_{ij}\eta_i\eta_j \right],$$

with the Coulomb integral

$$U_{ij} = \langle i,j | V_{ee} | i,j \rangle, \tag{6}$$

and

$$\overline{U_{\mathcal{M}}} = \frac{1}{N_{\mathcal{M}}^2}\sum_{i,j\in\mathcal{M}} U_{ij} = \frac{1}{(2l+1)^2}\sum_{i,j\in\mathcal{M}} U_{ij}, \tag{7}$$

whereby the U_{ij} vanish if i and j are belonging to different localized manifolds $\mathcal{M}$, containing $N_{\mathcal{M}}=\Sigma_{i\in\mathcal{M}}=2l+1$ strongly interacting electronic orbitals. As a consequence, each Kohn-Sham level is corrected by an amount,

$$\varepsilon_i = \frac{\partial E_{\text{LDA}+U}}{\partial \eta_i} = \varepsilon_{i\text{LDA}} + U_{ii}\left(\frac{1}{2} - \eta_i\right), \tag{8}$$

i.e., an orbital-dependent linear correction $U_{ii}(\frac{1}{2}-\eta_i)$ is provided that is able to recover the constant one-particle levels from the linear-dependent regime in the case of LDA, as sketched in the upper part of Fig. 1. In summary we have shown analytically that in the LDA+U formalism, the perfect recover of the constancy of the one-particle levels is provided by a set of perfect U values. The U values can be determined by a set of full self-consistent calculations on supercells with fractional electron numbers with U then chosen to cancel the slope of the LDA eigenvalues. In our work no Makov-Payne-type corrections are used because we think that using big supercells the interactions between charged defects can be reduced. Some residual error due to spurious charge-charge interactions becomes "wrapped up" in the U values. These considerations hold also in the case of strongly correlated electrons as shown numerically in Sec. III.

III. RESULTS AND DISCUSSION

A. Computational

The calculations are carried out with the DFTB calculation scheme which gives us the possibility to investigate charged systems in a very efficient way. In particular, with the use of very big supercells (512 atoms) the spurious interaction of charged defects with their periodic images can be reduced significantly. In addition the DFTB code allows for an empirical correction of the fundamental gap to the experimental value by optimizing the on-site Hubbard U that enters the tight-binding Hamiltonian.[8] Note that both properties appear to be necessary to obtain sufficiently well-described positions of the one-particle levels.

All numerical results were obtained by spin-polarized DFTB calculations. The spin configuration which minimizes the total energy was determined and used in each case. 512(256)-atom supercells of both hexagonal and cubic GaN containing one impurity (corresponding to a distance of 17.5 Å between defects in neighboring cells) were relaxed within the Γ approximation until the residual forces were lower than 10^{-4} eV/atom.

The substitutional Eu_{Ga} was also simulated with unrelaxed supercells in order to get results readily comparable with the literature. For each investigated system the position of the highest occupied orbital was calculated for occupation numbers from 0 to 1 with a step of 0.1, i.e., in 11 different points. The position of the transition levels is given with respect to the valence-band (VB) maximum (VBM). Since the VB edge in a supercell approach is not easy to determine,[16] an additional error bar of about 0.05–0.1 eV has to be taken into account. To analyze the linearity of the Kohn-Sham levels the *norm of the residuals* (mean-square deviation) between a linear fit and the calculated values is used,

$$\Delta = \frac{1}{n}\sqrt{\sum_{i=0}^{n}\{\varepsilon(x_i)^{\text{interpol.}} - \varepsilon(x_i)^{\text{calc.}}\}^2}, \tag{9}$$

where $x_i=(0.0,0.1,\ldots,1.0)$, and $\varepsilon^{\text{calc.}}$ and $\varepsilon^{\text{interpol.}}$ are the calculated and interpolated positions of the one-particle levels.

B. O_N and C_N in GaN

We first chose oxygen and carbon as representatives for the class of donor and acceptor impurities in GaN. Together with Si, oxygen is the standard impurity to dope GaN n type and is often an unintentional dopant.[17] Carbon has been suggested to be a convenient way to increase the hole concentration in GaN.[18] In recent experimental studies, C has been shown to be an alternative to Mg in order

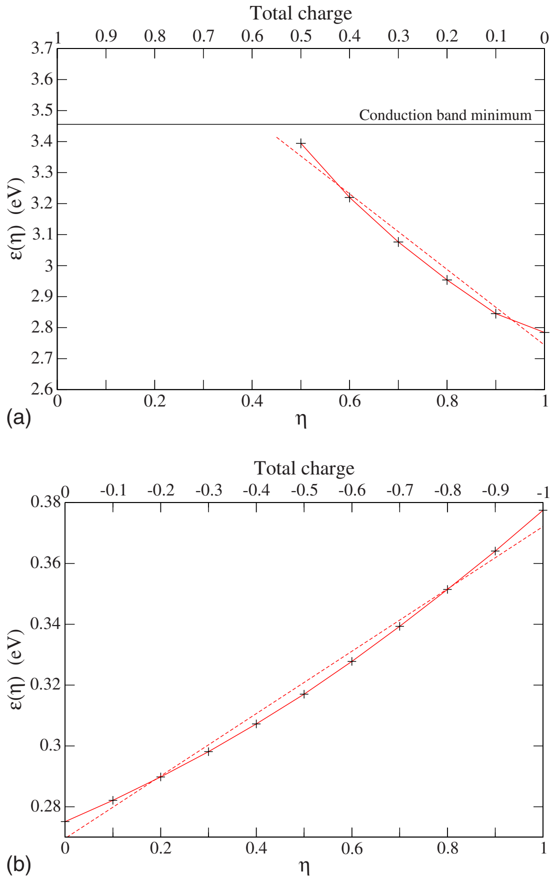

FIG. 2. (Color online) Highest occupied one-particle level as a function of its occupation for the O_N donor (upper box) and C_N acceptor (lower box) in hexagonal GaN (DFTB-LDA calculations). The dotted lines are linear interpolations of the calculated points. The zero of the energy scale corresponds to the VBM.

to obtain *p*-type-doped cubic GaN.[19] Both dopants have been frequently investigated experimentally and theoretically.[16,17,20–22] They are expected to be simple defects (both forming *N* substitutionals[17]) which at least in their ionized state (C_N^- and O_N^+) do not cause major distortion in the lattice due to their similarity (radius ad electronegativity) with the isoelectric substituted ion. C_N substitutionals lay on site independently from their charge state. However, according to the DFTB total-energy calculations, oxygen in the neutral charge state does not stay on site but occupies an off-center position instead. More precisely the O atom is displaced along the crystal *c* axis by 0.59 Å in the direction of the three equivalent Ga ligands. This configuration is 0.11 eV more favorable than the on-site configuration.

Due to the rather delocalized character of the wave functions, these defects should be already sufficiently well described within LDA for the calculation of the charge transition levels via the SJ transition state. In Fig. 2 the results of our LDA calculations of the (+/0) transition related to the substitutional O_N and of the transition (0/−) for the substitutional C_N in hexagonal GaN are compiled. First, we observe that in both cases the Kohn-Sham eigenvalues are roughly linear functions of the occupation η, as revealed by the nearly vanishing norm of residuals [see Eq. (9)], calculated in 7.336×10^{-3} and 0.981×10^{-3}, respectively. Second, in the case of O_N an increase in the occupation number of the one-particle level lowers its energy. Consequently the slope of the curve describing the position of this level depending from its occupation is negative, similar to negative-*U* systems. This is however the classic behavior of shallow donors. The charge transition levels for the hexagonal phase are calculated at 3.35 and 0.34 eV above the valence band for O_N and C_N, respectively, as reported in Table I. The same charge transitions in cubic GaN take place at very similar energies. This is in very good agreement with the existing data proving our assumption that these rather delocalized states can be properly analyzed using the model of a SJ transition state.[23]

C. V_N in GaN

The nitrogen vacancy in GaN is already discussed frequently in the literature as giving rise to negative-*U* transitions. Van de Walle and Neugebauer[17] calculated a (+3/+) transition to take place around 0.5 eV above the valence band, a value that later on based on increased supercell sizes was corrected by the same authors to be found somewhat closer to the VB maximum (around 0.3 eV). Only recently, Ganchenkova and Nieminen claimed the existence of transitions into negatively charged states.[24] Accordingly, a (+/−) negative-*U* transition is predicted to take place 2.46 eV above the valence-band edge.

In this work we investigate the negative-*U* transitions of V_N in hexagonal GaN with the help of the SJ transition state by carefully analyzing the charge states between +3 and − in the framework of LDA taking advantage of the empirically corrected gap. In the neutral charge state the nitrogen vacancy introduces a singly occupied a_1 state in the GaN band gap. Adding an electron the system is negatively charged and the localized state is doubly occupied, while subtracting one electron the system is positively charged and the level empty. First we check the linearity of this level with the occupation. The last two boxes in Fig. 3 show the position of the KS state calculated by adding and subtracting an electron. The norm of residuals Δ of these states (1.315×10^{-3} and 0.889×10^{-3}) shows their linear behavior. These pictures correspond to the transitions (+/0) and (0/−), respectively. The first is calculated at 2.90 eV and the second at 2.32 eV above the valence band. In other words, the transition (0/−) takes place *before* the transition (+/0). For the system is more convenient to charge the localized state directly with two electrons than with one missing out the charge state V_N^0 and giving rise to a direct transition from the positive into the negative charge state. This negative-*U* transition manifests itself also in an unusual negative slope of the position of the KS levels. The corresponding (+/−) transition can be easily calculated as the average of the charge transitions (+/0) and (0/−) resulting in a value of (2.90+2.32)/2=2.61 eV, in qualitative agreement with the value of 2.46 eV calculated in Ref. 24. The remaining discrepancy may be due to the fact that our approach provides an empirically corrected gap, thus leaving the one-particle level in question deep in the gap, whereas in the *ab initio* calculation this level is found artificially close to the too low lying LDA-conduction bands. The

TABLE I. Charge transition levels and slopes of the function $\varepsilon(\eta)=\alpha\eta+\beta$ for different systems. The levels are given in eV above the valence band. The slope α (in eV) and the mean-square deviation Δ according Eq. (9) have been calculated for the hexagonal phase. For completeness, the corresponding data for cubic GaN are also given. For the $+U$ parameters denoted by * the LDA$+U$ approach recovers the piecewise linearity of the one-particle levels of the Eu f orbitals.

System	Method	Structure	Transition	$\epsilon(0.5)$ hexagonal	$\epsilon(0.5)$ cubic	Slope α	$\Delta(\times 10^{-3})$
O_N	LSDA	Relaxed	$(+/0)$	3.35	3.35	−1.219	7.336
C_N	LSDA	Relaxed	$(0/-)$	0.32	0.34	−0.024	0.981
V_N	LSDA	Relaxed	$(0/-)$	2.31	2.35	−0.194	0.889
V_N	LSDA	Relaxed	$(+/0)$	2.89	3.26	−0.077	1.315
V_N	LSDA	Relaxed	$(2+/+)$	0.18	0.07	0.039	0.334
V_N	LSDA	Relaxed	$(3+/2+)$	0.15	0.09	0.014	0.120
Eu_{Ga}	LSDA	Ideal	$(0/-)$	2.83	2.81	1.990	42.340
Eu_{Ga}	LSDA	Relaxed	$(0/-)$	1.71	1.81	2.701	20.004
Eu_{Ga}	LSDA$+U$ (0.20 H)	Ideal	$(0/-)$	2.74	2.74	0.889	3.986
Eu_{Ga}	LSDA$+U$ (0.24 H)	Ideal	$(0/-)$	2.72	2.70	0.414	4.662
Eu_{Ga}	LSDA$+U$ (0.26 H)	Ideal	$(0/-)$	2.71	2.69	0.134	8.116
Eu_{Ga}	LSDA$+U$ (0.27 H) *	Ideal	$(0/-)$	2.70	2.69	−0.017	8.479
Eu_{Ga}	LSDA$+U$ (0.28 H)	Ideal	$(0/-)$	2.70	2.70	−0.169	9.523
Eu_{Ga}	LSDA$+U$ (0.22 H)	Relaxed	$(0/-)$	1.60	1.55	0.487	7.506
Eu_{Ga}	LSDA$+U$ (0.24 H)	Relaxed	$(0/-)$	1.60	1.55	0.115	4.036
Eu_{Ga}	LSDA$+U$ (0.25 H) *	Relaxed	$(0/-)$	1.58	1.54	−0.072	4.523
Eu_{Ga}	LSDA$+U$ (0.26 H)	Relaxed	$(0/-)$	1.58	1.53	−0.274	5.648
Eu_{Ga}	LSDA$+U$ (0.28 H)	Relaxed	$(0/-)$	1.57	1.52	−0.672	8.481

charge states +3, +2, and +1 almost give rise to a negative-U system, as the vacancy in the charge state +2 only can be formed if the Fermi levels lie in an interval which is only 0.003 eV wide. In this sense our results are in agreement with Ref. 17.

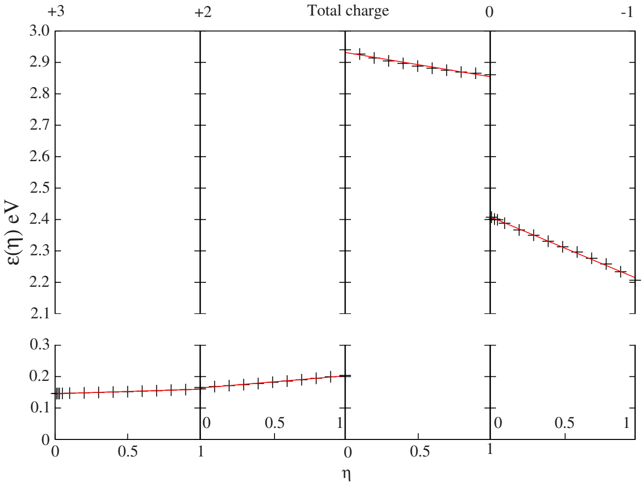

FIG. 3. (Color online) Highest occupied one-particle level as a function of its occupation for the different charge states of the isolated V_N in hexagonal GaN (DFTB-LDA calculations). The lines are linear interpolations of the calculated points. Note that the KS state in the first two boxes an s-like a_1 orbital is filled up step by step while the last two boxes are characterized by the p-like orbital derived from the splitting of the t_2 state in a doublet and a singlet in wurtzite GaN. The zero of the energy scale corresponds to the VBM.

The structure of the nitrogen vacancy changes a lot with the charge states: while in the charge state +1 the structure shows a (small) outward relaxation and the C_{3v} symmetry, in the charge states −1 is inward and the symmetry is D_{2d}, indicating a Jahn-Teller distortion. The distance between the Ga nearest neighbors is for the negative states very similar to the equilibrium Ga-Ga distance in bulk α-Ga and metallic-like Ga-Ga bonds have to be expected. The values of the norm of residuals Δ for the investigated systems indicate that the Kohn-Sham eigenvalues depend in first approximation linearly on the occupation numbers η. On the same time the minor deviations from the ideal values of 0.000 reveal a slight "concave" behavior, as already found by Göransson *et al.*[6] in the case of metallic alloys.

D. Eu_{Ga} in GaN

The RE_{Ga} substitutionals are the simplest stable lanthanide defects in GaN and in particular Eu_{Ga} has been already studied both experimentally[25] and theoretically.[26,27] In the latter work,[27] a charge transition related to an acceptor level (0/−) in cubic GaN was found at 2.44 eV above the valence band, whereby the strong localization of the Eu f electrons is taken into account within a self-interaction corrected (SIC) extension of LDA. In contrast, we present an LDA$+U$ investigation of this level, i.e., the nonlocal and energy-dependent self-energy is approximated by a frequency independent but nonlocal screened Coulomb potential.[9,10] The charge transition levels represent the position of the Fermi level at which a defect changes its charge

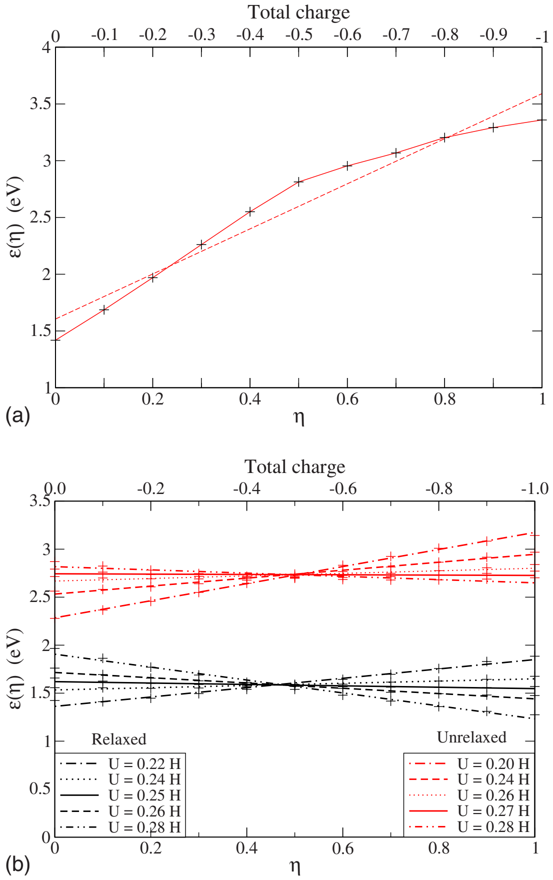

FIG. 4. (Color online) Highest occupied one-particle level as a function of its occupation for the $\mathrm{Eu}_{\mathrm{Ga}}$ substitutional in cubic GaN. In the first picture DFTB-LDA and in the second DFTB-LDA+U calculations. The lines are linear interpolations of the calculated data. In the second picture upper bunch of curves refer to calculations where the relaxation of the atomic positions is not considered and lower bunch of curves are calculated taking in account the atomic relaxation.

state. They are of course affected by variations of the relaxation due to the presence of additional electrons. In order to be able to compare our results directly with the SIC work of Svane *et al.*[27] for unrelaxed defect structures, we also provide an explicit discussion of the influence of the lattice relaxation. We start our discussion with an LDA investigation of the one-particle levels introduced in the band gap by the Eu impurity. As expected the dependence of the Kohn-Sham eigenvalues from the occupation cannot be really considered linear, it shows a rather pronounced convex behavior (see Fig. 4, left-hand side), reflected by a quite large norm of residuals ($\Delta = 42.340 \cdot 10^{-3}$). The situation becomes different with an LDA+U investigation. The orbital-dependent potentials introduced by LDA+U are used to correctly reproduce the separation between the two Hubbard subbands of full and empty f states with the parameter +U corresponding to the energy difference of the two bands. An estimate of the separation between the two Hubbard subbands is given by the Hubbard U of the atomic shell giving rise to the mentioned bands so that a first sensible choice for the correction is exactly the Hubbard U of the corresponding atomic shell. In this work the +U potentials are applied only to the Eu f shells. We used different +U values around the value of $\frac{1}{2}U_f$ calculated for the Eu atom using Janak's theorem, namely, 7.1 eV (0.26 H). This value is consistent with that used in recent works for similar simulations.[28,29]

The results of our calculation are reported in Fig. 4 (right-hand side): the f-related level introduced by the Eu impurity in the GaN band gap is now a linear function of the occupation number (Δ values between 3.986×10^{-3} and 9.523×10^{-3} for the unrelaxed defect and between 4.036×10^{-3} and 8.481×10^{-3} for the relaxed defect). The value of the correction for which the position Kohn-Sham level does not depend on its occupation η can be considered the ideal value for the manifold $\mathcal{M}$ of the Eu f electrons discussed in Eq. (6). This value does not only depend on the atomic species but also slightly from details of the system such as charge state and the microscopic structure (see also Fig. 4): Whereas for the ideal geometries the piecewise linearity of the total energy with respect to the total number of electrons is restored for a Hubbard U of 0.25 H, the corresponding value for the relaxed defect structure is given by $U = 0.27$ H. Note that in both cases the in this sense self-consistently determined value of the Hubbard U differs only slightly form the value of 0.26 H obtained from atomic calculations.

The position of the transition $(0/-)$ depends also slightly on the +U values and is calculated for hexagonal GaN and the relaxed structure at 1.58 eV above the band gap and at 2.70 eV above the band gap not considering the relaxation. The transition calculated for cubic GaN are only slightly lower whereby the one not considering the relaxation is in very good agreement with the value calculated by Svane *et al.*[27] for the ideal unrelaxed defect structure using the ΔSCF approach in combination with a SIC-functional.

IV. SUMMARY

In this work we demonstrate the validity of the Janak transition-state model, considered as an alternative way to the total-energy difference for the calculation of transition state. The charge transition levels have been calculated for different examples, including a selection of defects and impurities in GaN, besides oxygen donors (O_{N}) and carbon acceptors (C_{N}) also systems with negative-U effect (nitrogen vacancies, V_{N}) and those with strongly correlated electrons ($\mathrm{Eu}_{\mathrm{Ga}}$). Whereas in the latter case the linearity of the one-particle states with the occupation numbers is not provided in LDA, the application of the LDA+U approach recovers this linear dependence that is necessary for the SJ transition model to be applicable accurately. All numerical results are obtained by an approximate but efficient tight-binding approach that enables us to discuss the effect of the linearity of the eigenvalues separately while correcting the fundamental gap of GaN to the well-known experimental value. In this sense we reduce in part the predictive nature of the reference calculations. However, we are confident that the fundamental result, the validity of the Janak transition-state model, considered as an alternative way to the total-energy difference for the calculation of charge transition in connection with the LDA+U extension of DFT holds also for *first-principles* implementations of LDA+U. Even in cases when the band gap is not correctly described, the Slater-Janak transition state avoids the uncertainties (artificial Coulomb interaction) induced by comparing differently charged supercells. This benefit of the Slater-Janak transition state should be valid in connection with all extensions of the DFT including orbital-dependent potentials, not only LDA+U but also SIC, exact exchange, and especially the *GW* approximation. The latter approach should be perfectly suited to be combined with the SJ transition state since the quasiparticle approach leads to fundamental gaps and quasiparticle levels which are in reasonable agreement with the experiment.

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[1] G. Makov and M. C. Payne, Phys. Rev. B **51**, 4014 (1995).

[2] P. A. Schultz, Phys. Rev. Lett. **84**, 1942 (2000).

[3] U. Gerstmann, P. Deák, R. Rurali, B. Aradi, Th. Frauenheim, and H. Overhof, Physica B (Amsterdam) **340-342**, 190 (2003).

[4] J. F. Janak, Phys. Rev. B **18**, 7165 (1978).

[5] P. Mori-Sánchez, A. J. Cohen, and W. Yang, Phys. Rev. Lett. **100**, 146401 (2008).

[6] C. Göransson, W. Olovsson, and I. A. Abrikosov, Phys. Rev. B **72**, 134203 (2005).

[7] V. I. Anisimov, F. Aryasetiawan, and A. I. Lichtenstein, J. Phys.: Condens. Matter **9**, 767 (1997).

[8] T. Frauenheim, G. Seifert, M. Elstner, T. Niehaus, C. Kohler, M. Amkreutz, M. Sternberg, Z. Hajnal, A. Di Carlo, and S. Suhai, J. Phys.: Condens. Matter **14**, 3015 (2002).

[9] S. Sanna, B. Hourahine, Th. Gallauner, and Th. Frauenheim, J. Phys. Chem. A **111**, 5665 (2007).

[10] S. Sanna, B. Hourahine, U. Gerstmann, and Th. Frauenheim, Phys. Rev. B **76**, 155128 (2007).

[11] E. Rauls, Ph.D. thesis, Universität Paderborn, 2003.

[12] J. Elsner, M. Haugk, J. Jungnickel, and Th. Frauenheim, J. Mater. Chem. **6**, 1649 (1996).

[13] J. Elsner, R. Jones, M. I. Heggie, P. K. Sitch, M. Haugk, Th. Frauenheim, S. Oberg, and P. R. Briddon, Phys. Rev. B **58**, 12571 (1998).

[14] H. Eschrig, *The Fundamentals of Density Functional Theory* (Tuebner, Leipzig, 1996).

[15] M. Cococcioni and S. de Gironcoli, Phys. Rev. B **71**, 035105 (2005).

[16] J. Neugebauer and C. G. Van de Walle, Adv. Solid State Phys. **35**, 25 (1996).

[17] Ch. G. Van de Walle and J. Neugebauer, J. Appl. Phys. **95** 3851, (2004).

[18] C. R. Abernathy, J. D. Mackenzie, and S. J. Pearton, Appl. Phys. Lett. **66**, 1969 (1995).

[19] D. J. As and U. Köhler, J. Phys.: Condens. Matter **13**, 8923 (2001).

[20] P. Boguslawski and J. Bernholc, Phys. Rev. B **56**, 9496 (1997).

[21] I. Gorczyca, A. Svane, and N. E. Christensen, Phys. Rev. B **60**, 8147 (1999).

[22] L. E. Ramos, J. Furthmüller, L. M. R. Scolfaro, J. R. Leite, and F. Bechstedt, Phys. Rev. B **66**, 075209 (2002).

[23] C. G. Van de Walle, Phys. Rev. B **57**, R2033 (1998).

[24] M. G. Ganchenkova and R. M. Nieminen, Phys. Rev. Lett. **96**, 196402 (2006).

[25] K. P. O'Donnell and B. Hourahine, Eur. Phys. J.: Appl. Phys. **36**, 91 (2006), and references therein.

[26] J. S. Filhol, R. Jones, M. J. Shaw, and P. R. Briddon, Appl. Phys. Lett. **84**, 2841 (2004).

[27] A. Svane, N. E. Christensen, L. Petit, Z. Szotek, and W. M. Temmerman, Phys. Rev. B **74**, 165204 (2006).

[28] J. K. Lang, Y. Baer, and P. A. Cox, J. Phys. F: Met. Phys. **11**, 121 (1981).

[29] N. Singh, S. Mohan Saini, T. Nautiyal, and S. Auluck, Physica B (Amsterdam) **388**, 99 (2007).