Gaussian charge-transfer charge distributions for non-self-consistent electronic structure calculations

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We present a scheme to construct charge densities for non-self-consistent density functional theory calculations. Effects of charge transfer are added onto the density of overlapping atomic charge densities by means of charge-neutral spherical atom-centered Gaussian charge distributions that have been fitted to the self-consistent charge density in amorphous model systems. The electronic structure and forces obtained from non-self-consistent calculations using these a priori constructed charge densities are in good agreement with fully self-consistent calculations, and the Gaussian charge-transfer charges exhibit a satisfactory transferability between compounds of similar stochiometry but different geometry.

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I. INTRODUCTION

Conventional ab initio electronic structure calculations on large systems suffer from the fact that the effort to keep the occupied eigenstates of the single-particle Hamiltonian orthonormal scales cubically with respect to system size. In many cases, however, it might be sufficient to calculate a few selected eigenstates of the system: electronic and optical properties of semiconductor interfaces, for instance, are mainly determined by a limited number of states near the valence and conduction band edges and defect states within the forbidden gap. In a previous paper, we have shown that a combination of the generalized Davidson method and harmonic Ritz values (the harmonic Davidson algorithm) is well suited for solving large interior eigenvalue problems like the aforementioned.

The fact, however, that one does not compute all occupied eigenstates of a system means that it is not possible to reach self-consistency with respect to the electronic density. Consequently, to turn the above into a practical scheme, one needs (i) non–ab initio methods to optimize the geometry of large systems and (ii) an a priori scheme to construct charge densities, e.g., potentials, of sufficient quality for subsequent non-self-consistent density functional theory (DFT) calculations. This work addresses mainly the latter point.

As a crude first attempt, one could approximate the charge density of an arbitrary system by the overlapping atomic charges of its constituent atoms. In most systems (with the exception of monoatomic systems), however, this leads to a large overestimation of the band gap compared to a self-consistent calculation, primarily due to the complete neglect of charge transfer between the different inequivalent types of atoms in the system.

In the following we show that the effects of charge transfer may quite easily be added onto the density of overlapping atomic charges, by means of charge-neutral spherical atom-centered Gaussian charge distributions. Furthermore, we show that such Gaussian charge distributions may be determined by a nonlinear least-squares fit to the difference between the self-consistent charge density and the aforementioned density of overlapping atomic charges in amorphous model structures. The nonlinear least-squares fit is weighted such that the error in the Hartree energy is minimized.

Both the electronic structure and the forces obtained from non-self-consistent calculations using atomic charges plus these Gaussian charge-transfer charges (CTCs) are in quite reasonable agreement with fully self-consistent calculations, and the CTCs exhibit a satisfactory transferability. The latter we illustrate for α-Si3N4, β-Si3N4, and γ-Si3N4, using CTCs fitted for amorphous-Si3N4. It is our conjecture that this transferability to compounds of a different geometrical structure but similar stochiometry, is a result of the fact that we use amorphous structures to construct our CTCs.

Our scheme is reminiscent of the spherically approximated LDA (SLDA) potentials used by Chelikowsky and Cohen in their semiempirical pseudopotential method. SLDA potentials for a certain atomic type (or types) are constructed such as to approximately reproduce the local potential from self-consistent LDA calculations for these atoms in a set of systems with different geometrical structures and unit cell volumes. The resulting SLDA potentials for a certain atom are then averaged over the set. Structural averaging increases the transferability of the SLDA potentials. Analogously, we expect the transferability of the CTCs to benefit from the use of amorphous geometrical model structures.

We want to emphasize that neither density fitting by means of a least-squares minimization of the error in the Hartree energy nor the representation of charge densities through the use of spherical atom-centered Gaussian functions is a new technique (see, e.g., Refs. 6–11): the key point of the present work is the aforementioned use of amorphous geometrical model structures.

The remainder of this paper is organized as follows. Section II presents the definition of the aforementioned Gaussian CTCs. Computational details are discussed in Sec. III. In Sec. IV we compare the results of non-self-consistent band-structure calculations using atomic charges plus CTCs for α-Si3N4, β-Si3N4, γ-Si3N4, SiO2, GaAs, and AlAs, with their self-consistent counterparts, and we illustrate the benefits of constructing the CTCs using amorphous model structures. Section V addresses the quality of the forces obtained from non-self-consistent calculations using the CTC-corrected atomic charge densities. Finally, in Sec. VI we draw conclusions.
II. GAUSSIAN CHARGE-TRANSFER CHARGES

We fit the quantity

$$F(G_i) = \frac{\rho_{as}(G_i) - \rho_{at}(G_i)}{|G_i|},$$

(1)

where $\rho_{as}$ is the self-consistent charge density, $\rho_{at}$ is the overlapping atomic valence charge density of the reference atoms, and $G_i$ are the reciprocal lattice vectors, using the following function:

$$\mathcal{F}(G_i, \{Z_{nt}^t, \mu_n^t\}) = \sum_{t=1}^{N_t} \sum_{s=1}^{N_s} e^{G_i \cdot R'_t} \frac{N_s}{|G_i|} \sum_{n=1}^{N_n} Z_{nt}^t e^{-\frac{1}{2}(|\mu_n^t| G_i \cdot R'_t)}.$$  

(2)

Here the sum over $t$ is performed over all types of atoms, $s$ over the $N_t$ atoms of type $t$, and $n$ over the number of Gaussians per type ($2$ in our case). $R'_t$ is the position of atom $s$ of type $t$. Equation (2) may be rewritten as

$$\mathcal{F}(G_i, \{Z_{nt}^t, \mu_n^t\}) = \sum_{t=1}^{N_t} S_t(G_i) \sum_{n=1}^{N_n} Z_{nt}^t e^{-\frac{1}{2}(|\mu_n^t| G_i \cdot R'_t)},$$

(3)

with

$$S_t(G_i) = \sum_{s=1}^{N_s} e^{G_i \cdot R'_t} \frac{N_s}{|G_i|}.$$  

(4)

As a constraint we require that

$$\sum_{n=1}^{N_n} Z_{nt}^t = 0,$$

(5)
i.e., the Gaussian charge distributions carry no net charge per site.

In real space, the parameters $\{Z_{nt}^t, \mu_n^t\}$ define a charge density $\rho_{ctc}$, given by

$$\rho_{ctc}(r, \{Z_{nt}^t, \mu_n^t\}) = \frac{1}{(2\pi\epsilon_0)^3} \sum_{t=1}^{N_t} \sum_{n=1}^{N_n} Z_{nt}^t e^{-\frac{1}{2}(|\mu_n^t|^2)} \times \sum_{s=1}^{N_s} \exp \left[-\frac{1}{2} \left(\frac{|r - R'_t|}{\mu_n^t}\right)^2\right],$$

(6)

where $\rho_{ctc}$ approximates $\rho_{as} - \rho_{at}$ in a nonlinear least-squares sense, in such a way that the error in the Hartree energy is minimized (see the Appendix).

III. COMPUTATIONAL DETAILS

All results presented in this work were obtained using the Vienna Ab initio Simulation Package (VASP). Interactions between electrons and ions were treated using the projector-augmented-wave (PAW) method. For the constrained Levenberg-Marquardt nonlinear least-squares fits we used routines from the levmir library.

A. Si$_3$N$_4$

The unit cells of $\alpha$-Si$_3$N$_4$ (trigonal, space group P31c; No. 159), $\beta$-Si$_3$N$_4$ (hexagonal, space group P6$_3$mm; No. 173), and $\gamma$-Si$_3$N$_4$ (cubic spinel, space group Fd-3m; No. 227) contain 28, 14, and 14 atoms in their respective bases.

The structural parameters of $\alpha$-Si$_3$N$_4$, $\beta$-Si$_3$N$_4$, and $\gamma$-Si$_3$N$_4$ were taken from Refs. 16, 17, and 18, respectively. Since published internal coordinates from Rietveld analysis are usually not particularly accurate and lead to fairly large forces in ab initio calculations (in this case, about 1.0 eV/Å), the internal coordinates were optimized using the HSE06 hybrid functional.

The structure of amorphous Si$_3$N$_4$ (a-Si$_3$N$_4$) was constructed by melting a $2 \times 2 \times 4$ supercell of $\beta$-Si$_3$N$_4$ at 5500 K and cooling it down to 1500 K in steps of 500 K. At each temperature the system was put through $10^4$ steps of constant-volume molecular dynamics. The structure, obtained at 1500 K, was subsequently relaxed. Since the aforementioned procedure would be much too costly using the HSE06 hybrid functional, these calculations were done with the generalized-gradient-corrected density functional of Perdew-Burke-Ernzerhof (PBE).

Integrations over the first Brillouin zones of $\alpha$-Si$_3$N$_4$, $\beta$-Si$_3$N$_4$, and $\gamma$-Si$_3$N$_4$, to calculate the DOS and determine the self-consistent charge density used in subsequent self-consistent band structure calculations, were done on symmetry-reduced $\Gamma$-centered ($4 \times 4 \times 4$, $6 \times 6 \times 6$, and $6 \times 6 \times 6$) grids of $k$ points, respectively, using the improved tetrahedron method of Blöchl. The calculations on a-Si$_3$N$_4$ were done using the $\Gamma$ point only.

The determination of the CTCs and the electronic structure calculations on Si$_3$N$_4$ presented in the following were done using a plane-wave basis set with a kinetic energy cutoff of 400 eV. Exchange and correlation were treated using the local density approximation (LDA) of Ceperley and Alder. The fact that the crystalline and amorphous structures were optimized using the HSE06 and PBE functionals, instead of the LDA, has no bearing on our conclusions.

B. $\alpha$-SiO$_2$, GaAs, and AlAs

The structure of $\alpha$-SiO$_2$, with 9 atoms in the unit cell (space group P3$_{21}$; No. 154), was taken from Ref. 24. GaAs and AlAs crystallize in the zincblende structure (space group F43m; No. 216), with 2 atoms in the primitive cell. For GaAs and AlAs we assumed lattice constants of $a_0 = 5.468$ and 5.661 Å, respectively.

The amorphous SiO$_2$, GaAs, and AlAs structures were constructed using cubic supercells containing 243, 64, and 64 atoms, respectively, melting at 4000 K (a-SiO$_2$) and 4500 K (a-GaAs and a-AlAs), and cooling down to 2500 K (a-SiO$_2$) and 500 K (a-GaAs and a-AlAs) in steps of 500 K. Again, at each temperature the systems went through $10^4$ molecular dynamics steps, and the resulting structure at the lowest temperature was subsequently relaxed. All calculations on amorphous structures were done using the $\Gamma$ point only.

Calculation of the self-consistent charge densities used to fit the CTCs in a-SiO$_2$, a-GaAs, and a-AlAs, and the subsequent band structure calculations on $\alpha$-SiO$_2$, GaAs, and AlAs, were done using a plane-wave basis set with a kinetic energy cutoff of 400 eV (SiO$_2$) and 300 eV (GaAs and AlAs), respectively.

The self-consistent charge densities used in the calculation of the self-consistent band structures of SiO$_2$, GaAs, and AlAs were determined using symmetry-reduced $\Gamma$-centered ($6 \times 6 \times 6$) grids of $k$ points. For all calculations on SiO$_2$, A. Si$_3$N$_4$
GaAs, and AlAs, we used the PBE exchange-correlation functional.

IV. RESULTS

A. Si₃N₄

Figures 1–3 depict the band structure and DOS of α-Si₃N₄, β-Si₃N₄, and γ-Si₃N₄, calculated self-consistently (drawn lines) and non-self-consistently using charge densities made up of overlapping atomic charge densities plus CTCs fitted to the self-consistent charge density of a-Si₃N₄ (dotted lines). Clearly, the self-consistent band structure and DOS of α-Si₃N₄, β-Si₃N₄, and γ-Si₃N₄ are remarkably well reproduced by the non-self-consistent calculations using CTCs. The noticeable discrepancies between the self-consistent and non-self-consistent band structure of β-Si₃N₄ along Γ-M-K-Γ, especially near the top of the valence band, are due to the fact that we employ spherically symmetric CTCs. These bands are predominantly of N-p_z character. Using CTCs polarized along the z direction would lift these bands with respect to the neighboring bands of N-p_x and p_y character. For the latter the self-consistent and non-self-consistent band structures match quite nicely.

Table I lists the mean absolute energy difference Δ (in eV/state) between the eigenenergies of the states within a window of approximately 5 eV below the top of the valence band to 5 eV above the bottom of the conduction band in α-Si₃N₄, β-Si₃N₄, and γ-Si₃N₄, as obtained from self-consistent calculations and non-self-consistent calculations using CTCs fitted to the charge densities of a-Si₃N₄, α-Si₃N₄, β-Si₃N₄, and γ-Si₃N₄, labeled CTC(a), CTC(α), CTC(β), and CTC(γ), respectively. ⟨Δ⟩_av is the average over the three structures. Table I serves to illustrate the advantage of using CTCs fitted to the amorphous structure: (i) the CTC(a) CTCs perform uniformly well for all Si₃N₄ structures under consideration, and quite remarkably, (ii) the CTC(a) CTCs outperform the CTCs fitted to the particular structure itself.

The parameters [Z₁, μ₁, Z₂, and μ₂; see Eq. (6)] of the CTC(a) used in this work are listed in Table II. To investigate the stability of these parameters with respect to the amorphous structural models, we created a second a-Si₃N₄ model structure rapidly quenched from a molecular dynamics run at 3000 K.

### Table I. Mean absolute energy difference Δ (in eV/state) between the eigenenergies of states within approximately ±5 eV around the gap of α-Si₃N₄, β-Si₃N₄, and γ-Si₃N₄, from self-consistent calculations and non-self-consistent calculations using charge-transfer charges (CTCs) fitted to the charge densities of a-Si₃N₄, α-Si₃N₄, β-Si₃N₄, and γ-Si₃N₄, labeled CTC(a), CTC(α), CTC(β), and CTC(γ), respectively. ⟨Δ⟩_av is the average over the three structures.

<table>
<thead>
<tr>
<th>Structure</th>
<th>CTC(a)</th>
<th>CTC(α)</th>
<th>CTC(β)</th>
<th>CTC(γ)</th>
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<tr>
<td>α-Si₃N₄</td>
<td>0.046</td>
<td>0.048</td>
<td>0.226</td>
<td>0.267</td>
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<tr>
<td>β-Si₃N₄</td>
<td>0.057</td>
<td>0.135</td>
<td>0.113</td>
<td>0.060</td>
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<tr>
<td>γ-Si₃N₄</td>
<td>0.057</td>
<td>0.130</td>
<td>0.062</td>
<td>0.063</td>
</tr>
<tr>
<td>⟨Δ⟩_av</td>
<td>0.053</td>
<td>0.104</td>
<td>0.134</td>
<td>0.130</td>
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</tbody>
</table>

FIG. 1. Band structure and DOS of α-Si₃N₄ calculated self-consistently (solid lines) and non-self-consistently using CTCs from a-Si₃N₄ (dotted lines).

FIG. 2. Band structure and DOS of β-Si₃N₄ calculated self-consistently (solid lines) and non-self-consistently using CTCs from a-Si₃N₄ (dotted lines).

FIG. 3. Band structure and DOS of γ-Si₃N₄ calculated self-consistently (solid lines) and non-self-consistently using CTCs from a-Si₃N₄ (dotted lines).
 TABLE II. Parameters of the atom-centered, spherical, site-neutral Gaussian charge-transfer charges (two Gaussians per species; charge neutrality is achieved by imposing \( Z_1 = -Z_2 \)), fitted to the self-consistent charge densities of \( \alpha\)-Si\(_3\)N\(_4\), \( \alpha\)-SiO\(_2\), \( \alpha\)-GaAs, and \( \alpha\)-AlAs.

<table>
<thead>
<tr>
<th>( Z_1 )</th>
<th>( \mu_1 )</th>
<th>( Z_2 )</th>
<th>( \mu_2 )</th>
<th>( \mu^* )</th>
<th>( Z^* )</th>
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<td>Si</td>
<td>1444.098174</td>
<td>1.163507</td>
<td>1444.098174</td>
<td>1.163707</td>
<td>-1.163607</td>
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<tr>
<td>N</td>
<td>1629.323500</td>
<td>0.749452</td>
<td>-1629.323500</td>
<td>0.749789</td>
<td>-0.749621</td>
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<tr>
<td>Si</td>
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<td>-1194.780858</td>
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<td>-1.096668</td>
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<td>O</td>
<td>1303.752392</td>
<td>0.665854</td>
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<td>0.666143</td>
<td>-0.665999</td>
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<td>Ga</td>
<td>97.118165</td>
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<td>1.616839</td>
<td>-1.615180</td>
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<td>As</td>
<td>137.424521</td>
<td>1.150283</td>
<td>-137.424521</td>
<td>1.152193</td>
<td>-1.151238</td>
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<tr>
<td>Al</td>
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<td>1.525398</td>
<td>-93.768037</td>
<td>1.522063</td>
<td>-1.523731</td>
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<tr>
<td>As</td>
<td>198.615502</td>
<td>1.130008</td>
<td>-198.615502</td>
<td>1.131944</td>
<td>-1.130976</td>
</tr>
</tbody>
</table>

(molten \( \alpha\)-Si\(_3\)N\(_4\)). The CTC(a) parameters were found to be identical, within a few percent, to the \( \alpha\)-Si\(_3\)N\(_4\) CTC(a) parameters listed in Table II. This suggests that the parameters are stable and vary little when the amorphous model structure is changed, which is not particularly astonishing, since the number of fitted parameters is very small compared to the available information. We believe that the key benefit of using amorphous models is twofold. (i) First, the amorphous models contain distorted structural units, for instance, distorted SiN\(_4\) tetrahedra, as well as distorted NSi\(_3\) triangles, whereas the radial and angular distribution functions of the crystalline structures exhibit only a few sharp peaks. The availability of this additional information makes the fitting procedure well behaved, yielding unique parameters. (ii) The second key point is that amorphous models in a large supercell contain long-range information (corresponding to small \( G \) vectors) that is not available in a crystalline structure. In the past, authors have tried to increase the information content, by varying the lattice constants of the crystalline models or including different crystal structures in the fit. We have not tested this approach in the present work, since we believe that amorphous model structures allow for a more unbiased sampling of the relevant configuration space. Furthermore, variation of the crystalline structures hardly yields information on the long-range charge transfer. As an illustration, Fig. 4 shows the structure factor,

\[
S(G) = \begin{cases} \frac{1}{N_{atom}} \sum_{n=1}^{N_{atom}} \sum_{G=|\mathbf{G}|} |\epsilon^G \mathbf{R}_n|^2, & N(G) > 0 \\ 0, & N(G) = 0 \end{cases}, \tag{7}
\]

where \( N_{atom} \) is the number atoms per unit cell, \( \mathbf{R}_n \) are the atomic positions, and \( N(G) \) is the number of reciprocal lattice vectors of length \( G \), for \( \alpha\)-Si\(_3\)N\(_4\) and \( \alpha\)-SiO\(_2\), between \( G = 0 \) and 6 Å\(^{-1}\). For \( \alpha\)-Si\(_3\)N\(_4\), only a few peaks are visible, whereas for \( \alpha\)-Si\(_3\)N\(_4\), information is available at all reciprocal lattice vectors, even very short ones. We note that the situation would be even worse for simple cubic cells, for instance, the zinblende GaAs.

On account of the fact that \( Z_1 = -Z_2 \) and the Gaussian exponents \( \mu_1 \) and \( \mu_2 \) of the CTC(a) are almost equal, \( \rho_{\text{ctc}}(\mathbf{r}) \) (for an atom at \( \mathbf{r} = \mathbf{0} \)) may be accurately approximated by

\[
\mu^* = \frac{\mu_1 + \mu_2}{2}, \quad Z^* = \frac{\mu_2 - \mu_1}{\mu^*} Z_1, \tag{8}
\]

\[
\rho_{\text{ctc}}(\mathbf{r}) \approx \frac{Z^*}{(2\pi)^2} (3\mu^2 - |\mathbf{r}|^2) \exp \left[ -\frac{1}{2} \left( \frac{|\mathbf{r}|}{\mu^*} \right)^2 \right].
\]

The parameters \( \mu^* \) and \( Z^* \) are listed in Table II as well. As is apparent from Eq. (8), the linear combination of two almost-equal but opposite Gaussians yields a “quadrupole”-like charge distribution, with a node at \( |\mathbf{r}| = \mu^* \sqrt{3} \).

The radial distributions of the Si and N CTC(a) are depicted in Fig. 5. As one can clearly see in Fig. 5, the atom-centered CTCs of Si and N show a substantial contribution at neighboring sites: the nearest-neighbor distance in the different Si\(_3\)N\(_4\) structures is around 1.7–1.8 Å, and next-nearest neighbors (Si-Si and N-N) are found at approximately 3.0 Å.
Because of the fact that these radial distributions extend over several sites, it is hard to see from Fig. 5 what their accumulated effect in a particular structure would be. The latter is illustrated in Figs. 6–8.

Figure 6 shows $\rho_{ctc}$, the charge density from the spherical Gaussian CTC($\alpha$) in a [001] plane in $\beta$-Si$_3$N$_4$. As one clearly sees, the net effect is the transfer of charge from the Si sites (and quite diffusely out of the interstitial) onto the N sites. This is substantiated in more detail by Figs. 7 and 8. Figure 7 depicts the charge density difference $\rho_{sc} - \rho_{at}$, i.e., the self-consistent charge density minus the sum of overlapping atomic charge densities. The difference between $\rho_{sc}$ and $\rho_{at}$ is roughly consistent with the effect adding $\rho_{ctc}$ would have: compared to $\rho_{sc}$, $\rho_{at}$ does not yield enough charge on the N sites and leads to a surplus of electronic charge on Si and in the interstitial. Finally, the charge density difference $\rho_{sc} - \rho_{at} - \rho_{ctc}$, the self-consistent charge density minus the sum of overlapping atomic charge densities and CTCs, is shown in Fig. 8. As one may recognize from the latter, $\rho_{sc} - \rho_{at} - \rho_{ctc}$ has essentially no monopole on the atoms: the remaining differences after adding the CTCs consist of dipolar (or higher order) contributions at the atomic sites.

### B. SiO$_2$, GaAs, and AlAs

Figures 9–11 depict the band structure of $\alpha$-SiO$_2$, GaAs, and AlAs, calculated self-consistently (drawn lines) and non-self-consistently (dotted lines) using charge densities made up of overlapping atomic charge densities plus CTCs fitted to the self-consistent charge density of $\alpha$-SiO$_2$, a-GaAs, and a-AlAs, respectively. The parameters of the CTCs fitted to the self-consistent charge densities of $\alpha$-SiO$_2$, GaAs, and AlAs are listed in Table II. As was the case for the different phases of Si$_3$N$_4$, the agreement between self-consistent and

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**FIG. 5.** Spherical Gaussian charge-transfer charges for Si (solid line) and N (dashed line), fitted to the self-consistent charge density of a-Si$_3$N$_4$. Both charge distributions are centered at $r = 0$.

**FIG. 6.** Spherical Gaussian charge-transfer charge density ($e/\text{Å}^3$) in a [001] plane in $\beta$-Si$_3$N$_4$. Isolines are drawn at $-0.075$, $-0.05$, $0.0$, $0.1$, and $0.2$ eV/Å$^3$.

**FIG. 7.** Charge density difference ($e/\text{Å}^3$) $\rho_{sc} - \rho_{at}$, the self-consistent charge density minus the sum of overlapping atomic charge densities in a [001] plane in $\beta$-Si$_3$N$_4$. Isolines are drawn at $-0.15$, $-0.1$, $0.0$, $0.1$, $0.2$, and $0.3$ e/Å$^3$.

**FIG. 8.** Charge density difference ($e/\text{Å}^3$) $\rho_{sc} - \rho_{at} - \rho_{ctc}$, the self-consistent charge density minus the sum of overlapping atomic charge densities and CTCs in a [001] plane in $\beta$-Si$_3$N$_4$. Isolines are drawn at $-0.2$, $-0.1$, $-0.03$, $0.0$, $0.05$, $0.1$, and $0.2$ e/Å$^3$.

non-self-consistent band structures of $\alpha$-SiO$_2$, GaAs, and AlAs is remarkable.

V. FORCES

The CTC corrections to the atomic charge density also allow for the calculation of fairly accurate forces without the need for self-consistency. To demonstrate this, we list the phonon frequencies calculated for SiO$_2$ in Table III. Since the focus of this study is a comparison between self-consistent and non-self-consistent calculations, we do not show a comparison to experiment, although the agreement between DFT and experiment is fairly good, as shown in previous work. For the calculations presented here, we have used the experimental lattice parameters and the LDA to the exchange and correlation. The internal coordinates were relaxed for each method before calculating the phonon frequencies. A $4 \times 4 \times 4$ $k$-point grid was used, and the phonon frequencies were determined at the $\Gamma$ point only. In the case of a non-self-consistent calculation, additional contributions to the forces need to be calculated describing the change in the charge density (atomic charge density plus Gaussian CTCs) when the ions are moved.

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<th>Degeneracy</th>
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</tbody>
</table>
term was discussed in Ref. 12 and given by

$$\int \frac{\partial V_{\text{H}}(\rho_{\text{at}} + \rho_{\text{ctc}}) + V_{\text{xc}}(\rho_{\text{at}} + \rho_{\text{ctc}})(r)}{\partial R_n} \times (\rho[\psi](r) - \rho_{\text{at}}(r) - \rho_{\text{ctc}}(r))dr,$$  

where $R_n$ are the positions of the atoms, $V_{\text{H}}$ is the Hartree potential, $V_{\text{xc}}$ the exchange-correlation potential, $\rho_{\text{at}} + \rho_{\text{ctc}}$ the sum of overlapping atomic charge densities and Gaussian CTCs, and $\rho[\psi]$ the density calculated from the Kohn-Sham orbitals.

The first column in Table III shows the phonon frequencies from standard self-consistent calculations, the second column lists the results of non-self-consistent calculations that include the Gaussian CTCs, and the third column contains non-self-consistent calculations in which the density is approximated by overlapping atomic charge densities alone. The agreement between the self-consistent calculations and the non-self-consistent calculations using Gaussian CTCs is certainly not perfect but quite satisfactory. The average error is about 5%. If the charge density is calculated using overlapping atomic charge densities, agreement with the self-consistent calculations deteriorates and the mean absolute error increases from 30 to 50 cm$^{-1}$. Furthermore, the geometry predicted using only atomic charges deviates significantly from the self-consistent geometry, with a mean absolute error (MAE) of 0.3 Å, whereas the geometry predicted using additional Gaussian CTCs is in excellent agreement with the self-consistent geometry (an MAE of 0.015 Å). Similar results are obtained for AlAs, suggesting that the superposition of Gaussian-type CTCs and atomic charges indeed restores the most relevant properties of the self-consistent charge density, despite the fact that the spherical symmetry of the fragments is maintained.

VI. CONCLUSIONS

In the present paper we have shown how the effects of charge transfer and charge redistribution may be added onto the density of overlapping atomic charges by means of charge-neutral spherical atom-centered Gaussian charge distributions. These Gaussian charge distributions were determined by means of constrained nonlinear least-squares fits to the difference between the self-consistent charge density and the density of overlapping atomic charges in amorphous model structures. The electronic structures obtained from non-self-consistent calculations using overlapping atomic charge densities plus these Gaussian CTCs are in good agreement with the fully self-consistent calculations, and the Gaussian CTCs exhibit a satisfactory transferability between compounds of similar stoichiometry but different structure. The latter is a result of the fact that we use amorphous structures to construct these CTCs.

The use of amorphous model structures is the key point of the present work. Obviously all important properties of the self-consistent charge density are restored: the band structures as well as the forces are predicted reliably.

Two issues should be noted here. Creating an amorphous model structure might look like tedious work. With present-day resources, however, this is not the case. On a PC with four cores, about 10,000 molecular dynamics steps can be done in a single day, and reliable models can be constructed by equilibrating the system somewhat above the experimental melting point and performing one or two relaxations from this trajectory. The required human effort is a few hours (melting of a crystalline or a random structure at a very high temperature, 1000 time steps), equilibration of the structure about 20% above the experimental melting point (5000 time steps), and quenching of models into local minima using a conjugate gradient algorithm or some other local minimization algorithm (200 steps). Compared to crystalline reference structures, where structures and volumes and weights need to be set ad hoc, the present approach seems to be much simpler and less biased.

We believe that the present work is also fundamentally important. Our charge densities are made up of spherical fragments centered at the individual atomic sites. Remarkably, forces are very accurate: for instance, for GaAs and crystalline SiO$_2$ the relaxed structures are hardly distinguishable from structures relaxed using a fully self-consistent calculation (MAE, 0.015 Å), despite the fact that the non-self-consistent charge density lacks bond charges. Apparently, one only needs to restore the charge transfer and spherical rearrangement of the density at the atomic sites.

The final issue we want to note is that, for our plane-wave code, the savings in terms of computation time is typically only 50% compared to a fully self-consistent calculation. The main reason for the small gain is that VASP intermingles iterative matrix diagonalization and the self-consistency cycle, improving the charge density in a very efficient manner. In each iteration, the orbitals are improved only very little, so that little is gained when the charge update is skipped. This is, however, not the main direction of our future research. Once the need for a self-consistency cycle has been abandoned, it is possible to calculate only selected states close to the Fermi level (the Hamiltonian is fully determined by the density). In Ref. 4 we have shown that this allows calculations for structures containing 100,000 atoms in a couple of days, making the treatment of nanostructures possible, for instance, a GaAs nanodot embedded in an AlAs matrix. For these calculations, we constrain the calculations to a few selected states close to the conduction band minimum and valence band maximum, which often determine the electronic and optical properties.

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APPENDIX: NONLINEAR LEAST-SQUARES FIT

We minimize

$$R(x) = \frac{1}{2}f^T(x)f(x).$$  

Provided $f(x)$ has continuous second partial derivatives, we can write its Taylor expansion as

$$f(x + h) = f(x) + J(x)h + O(||h||^2).$$
In the Levenberg-Marquardt (damped Gauss-Newton) formulation of the nonlinear least-squares problem, the steps $h$ toward the minimum of Eq. (A1) is found from

$$(J^T J + \mu I)h = -J^T f,$$  \hspace{1cm} \text{with} \ \mu > 0, \hspace{1cm} (A3)$$

where the matrix $J$ is the Jacobian

$$J(x)_j = \frac{\partial f_j}{\partial x_j}(x),$$  \hspace{1cm} (A4)$$

and the weights

$$W_{ij} = \frac{1}{|G_i|^2} \delta_{ij}. \hspace{1cm} (A10)$$

This choice of weights prevents the sum of squared residual terms from becoming dominated by high Fourier components in the charge density. It weights the Fourier components of the density in accordance with their importance in the electrostatic Hartree energy. Remember that the Hartree potential $V_H$ due to a density $\rho$ is given by

$$V_H(G_i) = \frac{4\pi}{|G_i|^2} \rho(G_i).$$  \hspace{1cm} (A11)$$

As such, minimizing $R$ in Eq. (A6) amounts to the minimization of an error in the Hartree energy. In real space, the resulting Gaussian charge distribution corresponding to Eq. (A9) is given by Eq. (6).

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