Bond order potentials to include charge densities in TEM image interpretation

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The quantitative analysis of electron microscope images (conventional diffraction contrast TEM or high resolution HREM) requires image simulations of the object wave function (exit wave) based on well relaxed structure models and a suitable description of the electron scattering. The elastic interaction between electrons and an object can be simulated with good accuracy using the dynamical theory of electron interferences. Thereby the concept of structure factors is applied or the scattering potential $V(\vec{r})$ is given by solving the Poisson equation for the charge density. In order to calculate both the scattering potentials and the relaxed structure models molecular dynamics (MD) simulations have been performed, e.g. to study atomic processes related to the reordering at interfaces and the relaxation of nanostructures [1, 2]. From MD-relaxed structures TEM or HREM exit waves are simulated with the usual multi-slice formulation of the dynamical theory and applying Doyle-Turner or Weickenmeier-Kohl scattering potentials. In the present paper for small structures a comparison is made for simulations replacing the usual scattering structure description by potentials based directly on the charge density.

Ab initio calculations of $V(\vec{r})$ may be carried out by solving the one-electron Kohn-Sham equations for the crystal ground-state in the local density approximation, for the small structures considered here the code ABINIS [3] was applied. The charge density of the ground state yields directly the scattering potential and is equivalent to the three contributions: the Hartree energy for the valence electrons, the contribution of all effective nucleus potentials, and the exchange correlation effects. Such simulations on the first principle level may include quantum effects properly and describe the electronic properties completely, however, they are computationally too expensive for large systems. For larger systems only empirical molecular dynamics enable to calculate structure relaxations. However, the interatomic forces used in the empirical MD are accurate only if the influence of the local environment according to the electronic structure is included. Therefore it is important to have better approximations, such as the bond order or other well-constructed potentials, describing sufficiently accurate physical properties,which also give physical insights and enable a thorough understanding of the underlying processes.

The bond order potential (BOP) based on the tight binding (TB) model is used to enhance the MD, as it preserves the essential quantum mechanical nature of atomic bonding, yet abandons the electronic degree of freedom. TB and *ab initio* methods require complete diagonalisations of the Hamiltonian, which scale as $\mathcal{O}(N^3)$ and restrict MD to a few thousand atoms. The analytic BOP, however, achieves $\mathcal{O}(N)$ scaling by diagonalizing the orthogonal TB-Hamiltonian approximately and is recognized as a fast and accurate model for atomic interaction [4–6]. It allows to explore the dynamics of systems on macroscopic time and length scales on the atomic level that are beyond the realm of *ab initio* calculations.

The approximations to develop analytic BOP potentials from DFT may be summarized by the following steps: construct the TB matrix elements by Slater-Koster two-centre integrals including s- and p- orbitals, transform the matrix to the bond representation, replace the diagonalization by Lanczos recursion, obtain the momenta from the continued fraction representation of the Green function up to order n for an analytic BOPn potential. The total cohesive potential energy U_{coh} has three contributions: pair repulsion, promotion energy U_{prom}, and bond energy as excess of the band energy over the individual atomic interactions $U_{bond} = 2\sum_{i\alpha,j\beta}\Theta_{j\beta,i\alpha}H_{i\alpha,j\beta}$. In the BOP representation [5, 6] the matrix elements $H_{i\alpha,j\beta}$ are replaced by the Slater-Koster two-center integrals h_{ij} and the Goodwin-Skinner-Pettifor distance scaling function. The bond order $\Theta_{i\sigma,j\sigma}$ is equivalent to the electron density for which a concise analytical expression $\left[1 + \frac{N^2(\Phi^i_{2\sigma}+\Phi^j_{2\sigma})+\Phi^i_{2\sigma}\Phi^j_{2\sigma}(2N+\triangle\Phi_{4\sigma})}{(N+\triangle\Phi_{4\sigma})^2}\right]^{-1/2}$ can be given that employs the normalized second and fourth moment $(\Phi_{2\sigma}, \Phi_{4\sigma})$ of the local density of electronic states and $\triangle\Phi_{4\sigma} = (\Phi^i_{4\sigma} + \Phi^j_{4\sigma} - \Phi^{i2}_{2\sigma} - \Phi^{j2}_{2\sigma})/(\Phi^i_{2\sigma} + \Phi^j_{2\sigma})$, $N^2 = \triangle\Phi_{4\sigma} + \Phi^i_{2\sigma}\Phi^j_{2\sigma})$. The contribution $\Phi_{4\sigma}$ to the 4^{th} moment was given in terms of the matrix-elements of the tight binding Hamiltonian,

$$\sum_{k(i)\neq j} \hat{h}^4_{ik} g^2_{jik}, \qquad \sum_{\substack{k(i)\neq j \\ k'(k)\neq i,j}} \hat{h}^2_{ik}\hat{h}^2_{kk'} g^2_{jik} g^2_{ikk'}, \qquad {\sum_{k(i),k'(i)\neq j}}' \hat{h}^2_{ik}\hat{h}^2_{ik'} g_{jik} g_{kik'} g_{ik'}.$$

with the cosine of the bond angle $\mathcal{C}_{jik}$, the angular function $g_{ijk} = (1+\hat{p}_i\mathcal{C}_{jik})/(1+\hat{p}_i)$, reduced TB-parameters $\hat{p}_i = h_{pp\sigma}/h_{ss\sigma}$, and normalized hopping integrals $\hat{h}_{ik} = h_{ik}/h_{ij}$ etc.

The resulting semi-empirical many body potential is transferable to describe phases and configurations not included in the parameter fit, a feature not found in other empirical potentials. Moreover, transferability extends to different kinds of materials, where only the parameters need to be refitted. In the implementation of the enhanced BOP4+ a number of angular terms are included that are related to certain π bonds between neighboring atoms and contribute up to 40%, but were ignored previously. With the angle of torsion $\mathcal{C}_{ij,kk'}$ and the abbreviations $\mathcal{Z} = \mathcal{C}_{ij,kk'} + \mathcal{C}_{jik}\mathcal{C}_{ikk'}$ and $\xi = \hat{\pi}_i\hat{p}_k/(1+\hat{p}_i)$ one yields the new contribution to the 4-th momentum:

$$\sum_{\substack{k(i)\neq j \\ k'(k)\neq i,j}} \hat{h}^2_{ik}\hat{h}^2_{kk'}\mathcal{Z}\xi\left(\frac{\mathcal{Z}\xi}{(1+\hat{p}_k)^2} + \frac{2g_{jik}g_{ikk'}}{1+\hat{p}_k}\right).$$

Similarly on-site contributions to $\Phi_{4\sigma}$ proportional to the energy splitting δ_i are included $\sum \hat{h}^2_{ik}\left\{g_{jik}(2\hat{\delta}^2_i + \hat{\delta}^2_k) + \hat{p}_i\hat{\delta}^2_i\frac{(1-\mathcal{C}_{jik})^2}{(1+\hat{p}_i)^2}\right\} + \hat{\delta}^4_i$.

The improved BOP4+ allows nanoscopic structure calculations including electronic properties. Besides an accurate fit, the BOP requires well parameterized TB matrix elements or parameter optimizing, and the problem of transferability have to be considered separately. For BOP of order n = 2 the bond-order term looks like a Tersoff potential and the numerical behavior of BOP2 and the empirical Tersoff potential are approximately equivalent. The details for the enhanced analytic BOP4+ will be given in more details elsewhere, complicated angular terms occur, reflecting the non-radial electronic structure of the bonds.

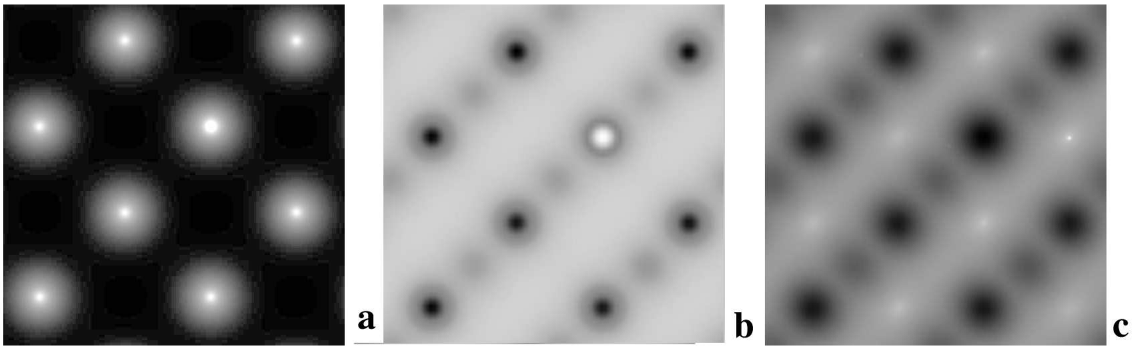

Fig. 1 Phase grating of a central slice with thickness 1.358nm located in a depth of 4.753 nm for a Si[100] structure with two Ge substitutional atoms: a) structure factor model, b) DFT charge density, c) scanned BOP

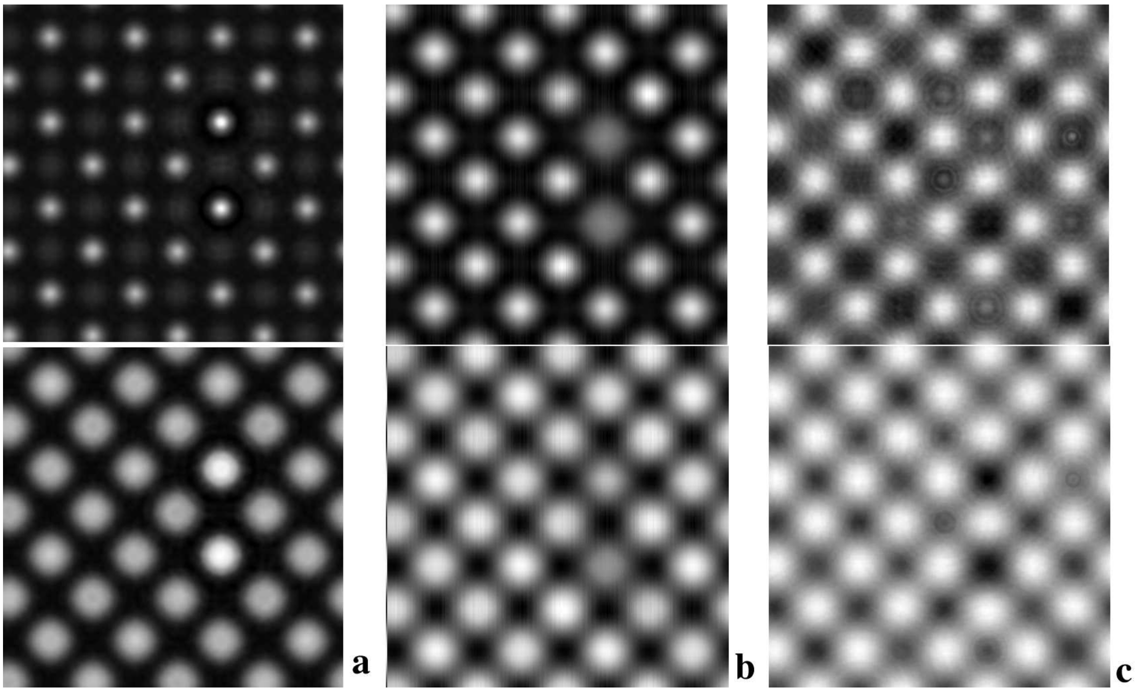

Fig. 2 Amplitudes (upper row) and phases (lower row) of the exit wave for a Si[100] structure with two Ge substitutional atoms at an object thickness of 5.432 nm: a) structure factor model, b) DFT charge density, c) scanned BOP

As an first and simple example, the exit wave in [100] projection is calculated for a 2x2x2 supercell of silicon containing two germanium substitutional atoms. The supercell (1.086nm box length) is sliced into 8 different slices of 1.358nm thickness. The simulations using the Doyle-Turner scattering factors are compared with calculations for potentials derived from DFT charge densities and those using scanned BOP4+ potentials. Fig.1 shows the phase grating of a central slice of the object, the Ge atoms are indicated by the modified scattering potential within this slice. The different approximations - cf. Figs.1 a, b, and c for the structure factor model, the DFT charge density, and the scanned BOP4+, respectively - give a different influence of the electronic structure in the phase grating. The structure factor model is represented always by spherical symmetrical scattering potentials around the scatterers, whereas for the other approximations the phase grating is influenced by the angular behaviour of the bond structure. Using the multi-slice algorithm with the 8 different slices the amplitudes and phases of the exit wave are calculated for a thickness of 5.432 nm (5x8 = 40 slices) in Fig.2. The different potential models do not modify the exit wave as strong as the phase grating, but may be revealed especially in the phase of the waves. The detailed investigation of the contrast influences, the refinement of the simulations, and the application of large supercells containing lattice defects will be the matter of work in progress.

[1] K. Scheerschmidt and P. Werner, In: *Nano-Optoelectronics: Concepts, Physics and Devices*, Ed. M. Grundmann (Springer, Berlin 2002) Chapter 3, pp. 67-98
[2] K. Scheerschmidt and V. Kuhlmann, Interface Sci. **12**, 157 (2004)
[3] X. Gonze, J.-M. Beuken, R. Caracas, et al. Computational Materials Science **25**, 478 (2002)
[4] M.W. Finnis: *Interatomic Forces in Condensed Matter*, Oxford Series on Materials Modelling (Oxford University Press, Oxford, 2003)
[5] A.P. Horsfield, A.M. Bratovsky, M. Fear, et al., Phys. Rev. B **53**, 19 (1996);
[6] D.G. Pettifor, M.W. Finnis, D. Nguyen-Manh, et al., Mat. Sci. Eng. A, **365**, 2 (2004)