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TOWARDS A COHERENT TREATMENT OF THE SELF-CONSISTENCY AND THE ENVIRONMENT-DEPENDENCY IN A SEMI-EMPIRICAL HAMILTONIAN FOR MATERIALS SIMULATION

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The construction of semi-empirical Hamiltonians for materials that have the predictive power is an urgent task in materials simulation. This task is necessitated by the bottleneck encountered in using density functional theory (DFT)-based molecular dynamics (MD) schemes for the determination of structural properties of materials. Although DFT/MD schemes are expected to have predictive power, they can only be applied to systems of about a few hundreds of atoms at the moment. MD schemes based on tight-binding (TB) Hamiltonians, on the other hand, are much faster and applicable to larger systems. However, the conventional TB Hamiltonians include only two-center interactions and they do not have the framework to allow the self-consistent determination of the charge redistribution. Therefore, in the strictest sense, they can only be used to provide explanation for system-specific experimental results. Specifically, their transferability is limited and they do not have predictive power. To overcome the size limitation of DFT/MD schemes on the one hand and the lack of transferability of the conventional two-center TB Hamiltonians on the other, there exists an urgent need for the development of semi-empirical Hamiltonians for materials that are transferable and hence, have predictive power.

The key ingredient to the development of semi-empirical Hamiltonians for materials that have predictive power is a reliable and efficient scheme to mimic the effect of screening by electrons when atoms are brought together to form a stable aggregate. Such an ingredient requires the construction of

the semi-empirical Hamiltonian based on a framework that allows a coherent treatment of the self-consistent (SC) determination of charge redistribution and environment-dependent (ED) multi-center interactions. Various schemes can be found in the literature in recent years that are designed to improve the transferability of TB Hamiltonians by including the self-consistency and/or the environment-dependency. Among these are methods that can also be conveniently implemented in MD schemes because the atomic forces can be readily calculated. They include methods whose emphasis is placed on a phenomenological description of the environment-dependency [1, 2] and two similar methods whose frameworks take into account the self-consistency as well as the environment-dependency [3, 4]. The latter two approaches can be construed as the expansion of the DFT-total energy in terms of the charge density fluctuations about some reference density. To the second order in the density fluctuations, the total energy is approximated as the sum of a band structure term, a short-range repulsive term akin to that in the conventional two-center TB Hamiltonian, and a term representing the Coulomb interaction between charge fluctuations. The charge fluctuations in this approach are self-consistently determined by solving an eigenvalue equation with the two-center Hamiltonian modified by a term that depends on the charge redistribution. In this framework, the Hamiltonian does contain the features of self-consistency in the charge redistribution and the environment-dependency for systems with charge fluctuations. The environment-dependent feature, however, disappears when systems under consideration do not involve charge fluctuations, e.g., periodic systems with one atomic species per primitive unit cell. But the environment-dependent multi-center interactions are key features in a realistic modeling of the screening effect of the electrons in an aggregate of atoms, including extended periodic systems. This deficiency in properly mimicking the screening of the electrons can be critical in the development of a truly transferable Hamiltonian. Thus the development of semi-empirical Hamiltonians for materials with predictive power requires the treatment of the self-consistency as well as the environment-dependency on equal footing.

We have recently developed a scheme for the construction of semi-empirical Hamiltonians for materials within the framework of linear combination of atomic orbitals (LCAO) that allows a coherent treatment of the SC determination of the charge redistribution and the environment-dependent (ED) multi-center interactions in a transparent manner [5]. In this scheme, we set up the framework of the semi-empirical Hamiltonian in accordance with the Hamiltonian of the many-atom aggregate. The salient feature of the resulting semi-empirical Hamiltonian, referred as the SCED/LCAO Hamiltonian, is that it has the flexibility to allow the database to provide the necessary ingredients for fitting parameters to capture the effect of electron screening.

The Hamiltonian of a many-atom aggregate may be written as

$$H = -\sum_l \frac{\hbar^2}{2m}\nabla_l^2 + \sum_{l,i} v(\vec{r}_l - \vec{R}_i) + \sum_{l,l'} \frac{e^2}{4\pi\varepsilon_0 r_{ll'}} + \sum_{i,j} \frac{Z_i Z_j e^2}{4\pi\varepsilon_0 R_{ij}} \qquad (1)$$

where $v(\vec{r}_l - \vec{R}_i)$ is the potential energy between an electron at $\vec{r}_l$ and the ion at $\vec{R}_i$, $r_{ll'} = |\vec{r}_l - \vec{r}_{l'}|$, $R_{ij} = |\vec{R}_i - \vec{R}_j|$, and Z_i corresponds to the number of valence electrons associated with the ion at site $\vec{R}_i$. Within the one-particle approximation in the framework of LCAO, the on-site (diagonal) element of the Hamiltonian can be written as

$$H_{i\alpha,i\alpha} = \varepsilon_{i\alpha}^0 + u_{i\alpha}^{\text{intra}} + u_{i\alpha}^{\text{inter}} + v_{i\alpha} \qquad (2)$$

where $\varepsilon_{i\alpha}^0$ denotes the sum of the kinetic energy and the energy of interaction with its own ionic core of an electron in the orbital $i\alpha$. The terms $u_{i\alpha}^{\text{intra}}$ and $u_{i\alpha}^{\text{inter}}$ are the energies of interaction of the electron in orbital $i\alpha$ with other electrons associated with the same site i and with other electrons in orbital $j\beta$ ($j \neq i$), respectively. The term $v_{i\alpha}$ represents the interaction energy between the electron in orbital α at site i and the ions at the other sites. In our scheme, the terms in Eq. (2) are represented by

$$\varepsilon_{i\alpha}^0 = \varepsilon_{i\alpha} - Z_i U \qquad (3)$$

$$u_{i\alpha}^{\text{intra}} = N_i U \qquad (4)$$

and

$$u_{i\alpha}^{\text{inter}} + v_{i\alpha} = \sum_{k \neq i} [N_k V_N(R_{ik}) - Z_k V_Z(R_{ik})] \qquad (5)$$

where $\varepsilon_{i\alpha}$ may be construed as the energy of the orbital α for the isolated atom at i, Z_i the number of positive charges carried by the ion at i (also the number of valence electrons associated with the isolated atom at i), N_i the number of valence electrons associated with the atom at i when the atom is in the aggregate, U, a Hubbard-like term, the effective energy of electron-electron interaction for electrons associated with the atom at site i, $V_N(R_{ik})$ the effective energy of electron-electron interaction for electrons associated with different atoms (atoms i and k), and $Z_k V_Z(R_{ik})$ the effective energy of interaction between an electron associated with an atom at i and an ion at site k.

Following the same reasoning, we can set up the off-diagonal matrix element $H_{i\alpha,j\beta}$ $(j \neq i)$ as

$$H_{i\alpha,j\beta} = \frac{1}{2}\left\{ K(R_{ij})(\varepsilon'_{i\alpha} + \varepsilon'_{j\beta}) + [(N_i - Z_i) + (N_j - Z_j)]U \right.$$

$$+ \left[\sum_{k \neq i}(N_k V_N(R_{ik}) - Z_k V_Z(R_{ik})) \right.$$

$$\left. \left. + \sum_{k \neq j}(N_k V_N(R_{jk}) - Z_k V_Z(R_{jk})) \right] \right\} S_{i\alpha,j\beta}(R_{ij}) \qquad (6)$$

Thus, in addition to the conventional two-center hopping-like first term, Eq. (6) also includes both intra- and inter-electron-electron interaction terms as well as environment-dependent multi-center (three-center explicitly and four-center implicitly) interactions.

In its broadest sense, the first term in Eq. (6) corresponds to the Wolfsberg–Helmholtz relation in the extended Hückel theory. In our approach, K is treated as a function of R_{ij} rather than a constant parameter to ensure a reliable description of the dependence of the two-center term on R_{ij} in the off-diagonal Hamiltonian matrix element. The overlap matrix elements $S_{i\alpha,j\beta}(R_{ij})$ are expressed in terms of $S_{ij,\tau}$, with τ denoting, for example, molecular orbitals $ss\sigma$, $sp\sigma$, $pp\sigma$, and $pp\pi$ in a sp^3 configuration. They are expected to be short-ranged function of R_{ij}.

Equations (2) through (6) completely define the recipe for constructing semi-empirical SCED-LCAO Hamiltonians for materials in terms of parameters and parameterized functions. An examination of Eqs. (2)–(6) clearly indicates that the presence of N_i, the charge distribution at site i, in the Hamiltonian provides the framework for a self-consistent determination of the charge distribution. From Eqs. (5) and (6), it can be seen that the environment-dependent multi-center interactions are critically dependent on $V_N(R_{ik})$ and $V_Z(R_{ik})$, in particular their difference $\Delta V_N(R_{ik}) = V_N(R_{ik}) - V_Z(R_{ik})$. As both $V_N(R_{ik})$ and $V_Z(R_{ik})$ must approach E_0/R_{ik} for R_{ik} beyond a few nearest neighbor separations, $\Delta V_N(R_{ik})$ is expected to be a short ranged function of R_{ik}. The parameters, including those characterizing the parameterized functions, are to be optimized with respect to a judiciously chosen database for a particular material. In our approach, $\varepsilon_{i\alpha}$ may be chosen according to its estimated value based on the orbital $i\alpha$, or treated as a parameter of optimization. The quantity U will be treated as a parameter of optimization while $V_Z(R_{ik})$ and $V_N(R_{ik})$ will be treated as parameterized functions to be optimized. The parameterized function $V_Z(R_{ik})$ is modeled as the energy of the effective interaction per ionic charge between an ion at site k and an electron associated with the atom at site i. $V_N(R_{ik})$ is then modeled in terms of $V_Z(R_{ik})$ and the short-range function ΔV_N.

The recognition of the difference between $V_N(R_{ik})$ and $V_Z(R_{ik})$ in the SCED/LCAO Hamiltonian assures that the environment-dependent feature will not disappear even for systems with no charge redistribution. The presence of the environment-dependent terms in the SCED/LCAO Hamiltonian for systems with no on-site charge redistribution affects the distribution of the electrons among the orbitals even though the total charge associated with a given site is not changed. Therefore, the effect of the environment-dependency will be reflected in the band structure energy through the solution to the general eigenvalue equation corresponding to the SCED/LCAO Hamiltonian as well as the total energy. This feature, together with the self-consistency in the determination of the charge redistribution, provides the flexibility for the SCED/LCAO Hamiltonian to mimic the effect of electron screening.

According to the strategy given above, the framework of the proposed semi-empirical SCED-LCAO Hamiltonian will allow the self-consistent determination of the electron distribution at site i. The inclusion of environment-dependent multi-center interactions will provide the proposed Hamiltonian with the flexibility of treating the screening effect associated with electrons which is important for the structural stability of narrow band solids such as d-band transition metals, while at the same time, handling the effect of charge redistribution for systems with reduced symmetry on equal footing. Furthermore, as described above, the Hamiltonian is set up in such a way that the physics underlying each term in the Hamiltonian is transparent. Therefore, it will be convenient to trace the underlying physics for properties of a system under consideration when such a Hamiltonian is used to investigate a many-atom aggregate and predict its properties. The salient feature of our strategy is that, with the incorporation of all the relevant terms discussed previously, there is no intrinsic bias towards ionic, covalent, or metallic bonding for the proposed Hamiltonian. The construction of the SCED/LCAO Hamiltonian depends critically on the database. If one can judiciously compile a systematic and reliable database, the scheme has the flexibility to allow the database to properly model the screening effect of the electrons in an atomic aggregate. Thus the strategy represents an approach that provides the appropriate conceptual framework to allow the chemical trend in a given atomic aggregate to determine the structural as well as electronic properties of condensed matter systems.

The total energy of the system consistent with the Hamiltonian described by Eqs. (2)–(6) is given by

$$E_{\text{tot}} = E_{BS} - E_{\text{corr}} + E_{\text{ion-ion}} \tag{7}$$

where E_{BS} is the band-structure energy and is obtained by solving the general eigenvalue equation corresponding to the SCED/LCAO Hamiltonian, E_{corr} is the correction to the double counting of the electron-electron interactions between the valence electrons in the band-structure energy calculation, and

$E_{\text{ion}-\text{ion}}$ is the repulsive interaction between ions. Based on Eqs. (2)–(6), Eq. (7) can be rewritten as

$$E_{\text{tot}} = E_{BS} + \frac{1}{2}\sum_i (Z_i^2 - N_i^2)U - \frac{1}{2}\sum_{i,k(i \neq k)} N_i N_k V_N(R_{ik})$$
$$+ \frac{1}{2}\sum_{i,k(i \neq k)} Z_i Z_k V_C \qquad (8)$$

with

$$V_C = \frac{e^2}{4\pi\,\varepsilon_0 R_{ik}} = \frac{E_0}{R_{ik}} \qquad (9)$$

For the MD simulation, the forces acting on the atoms in the atomic aggregate must be calculated at each MD step. The calculation of the band structure contribution to atomic forces can be carried out by the Hellmann–Feynman theory. With the presence of terms involving N_i and N_k in the SCED-LCAO Hamiltonian (see Eqs. (5) and (6)), terms such as $\nabla_k N_i$ where ∇_k refers to the gradient with respect to $\vec{R}_k$ will appear in the electronic contribution to the atomic forces. However, these terms are canceled exactly by terms arising from the gradients of the second and the third terms in the total energy expression (Eq. (8)). Thus terms involving $\nabla_k N_i$ will not contribute to the calculation of atomic forces. This fact greatly simplifies the calculation of atomic forces needed in the MD simulations. In other words, if one disregards the extra time due to the self-consistency requirement, the calculation of atomic forces based on the SCED–LCAO Hamiltonian is not anymore difficult compared with conventional TB approaches.

We have tested the SCED/LCAO Hamiltonian by investigating a variety of different structures of silicon (Si), including the bulk phase diagrams of Si, the equilibrium structure of an intermediate-size Si_{71} cluster, the reconstruction of the Si(100) surface, and the energy landscape for a Si monomer adsorbed on the reconstructed Si(111)-7×7 surface [5]. In all the cases studied, the results have demonstrated the robustness of the SCED/LCAO Hamiltonian. For example, results showing the binding energy *vs* relative atomic volume curves for the diamond, the simple cubic (sc), the body centered cubic (bcc), and the face centered cubic (fcc) phases of silicon, obtained by using the SCED–LCAO Hamiltonian constructed for Si with our scheme, are presented in Fig. 1. Also shown in Fig. 1 are the corresponding curves obtained using three existing traditional (two-center and non-self consistent) non-orthogonal tight binding (NOTB) Hamiltonians [6–8], and two more recently developed non-self consistent but environment-dependent Hamiltonians [1, 2]. All the curves (solid) are compared with the results obtained by DFT–LDA calculations [9].
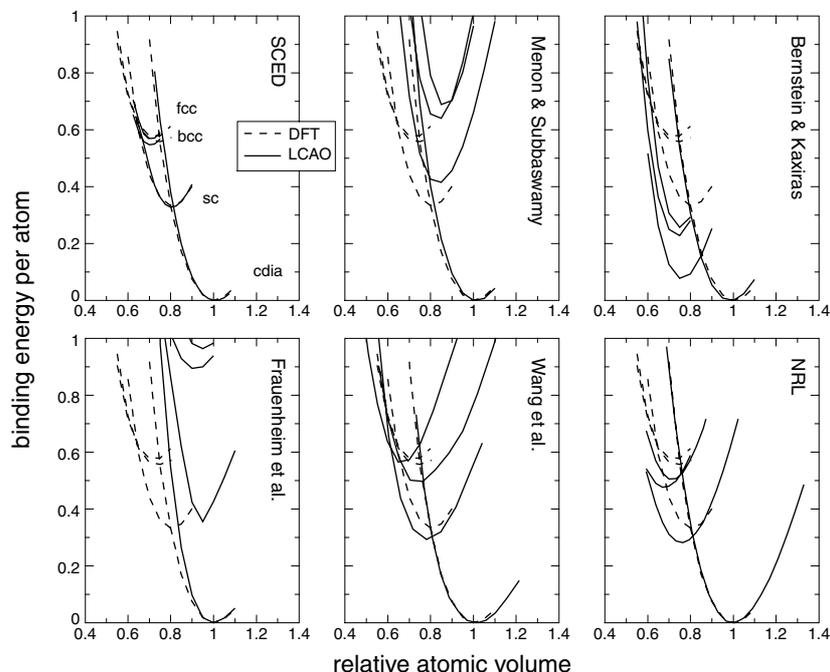
Figure 1. The binding energy versus relative atomic volume curves for the diamond (cdia), the simple cubic (sc), the body centerd cubic (bcc), and the face centered cubic (fcc) phases of silicon. Top-left panel: SCED-LCAO Hamiltonian. Top-central panel: [7]; Top-right panel: [8]; Bottom-left panel: [6]; Bottom-central panel: [1]; Bottom-right panel: [2]. All the curves (solid) are compared with the result obtained by a DFT–LDA calculation [9].

It can be seen that while the results obtained by all the existing Hamiltonians fail for the high pressure phases, those obtained using Hamiltonians with environment-dependent terms give much better agreement for those phases. This is an indication of the importance of the inclusion of the environment-dependent effects in the Hamiltonian, even for single-element extended crystalline phases where there is no charge redistribution. However, the most striking message conveyed by Fig. 1 is how well our result compares with the DFT–LDA results for all the extended crystalline phases, both at low as well as high pressures. It indicates that the SCED/LCAO Hamiltonian has the capacity and the flexibility of capturing the environment-dependent screening effect under various local configurations.

The framework of the SCED/LCAO Hamiltonian outlined in Eqs. (2)–(6) is very flexible. It can be conveniently extended to include the spin-polarized effect and to construct SCED/LCAO Hamiltonians for heterogeneous systems in terms of parameters of SCED/LCAO Hamiltonians of their constituent elemental systems. Work along these lines is in progress.

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