

An integral-equation approach to the electronic structure of liquid silicon

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Abstract. We have extended an integral-equation approach (proposed by Winn and Logan, and, in parallel, by Stratt and co-workers) for the determination of the electronic density of states of disordered materials within the ‘tight-binding’ framework to the case of an sp^3 model. This formalism leads to a set of coupled complex-valued integral equations which turn out to be formally equivalent to the Ornstein–Zernike equations of an ion–dipole mixture. As a closure relation, which is required for the solution, we have used a linear relation. In order to check the reliability of this approach we have complemented the integral-equation data with results from a ‘tight-binding’ molecular-dynamics simulation. As an example we chose liquid silicon, using the ‘tight-binding’ parametrization proposed by Goodwin *et al.* The agreement of the two sets of data is very satisfactory.

1. Introduction

An integral-equation approach for the determination of the electronic structure of disordered materials, proposed several years ago by Winn and Logan [1–3] and Stratt and co-workers [4] has turned out to be an appealing and reliable tool for the determination of the electronic density of states (DOS) of liquid and amorphous materials. Based on one hand on a ‘tight-binding’ (TB) model for the electronic interaction and on the other hand on the structure of the disordered system in terms of the pair distribution function (PDF) $g(r)$, the formalism leads to a complex-valued Ornstein–Zernike- (OZ-) type integral equation which has to be solved together with a closure relation. From the solution of these equations it is then possible to determine the electronic structure in terms of the DOS. Implementations of this approach have been realized both for the one-band [5, 6] and the two-band model [5] using the linear ‘single-superchain’/‘effective-medium’ approximation (SSCA/EMA).

In principle, it is straightforward to extend this integral equation to the four-band (sp^3) model: it turns out that the resulting set of integral equations is formally equivalent to the OZ equations for an ion–dipole mixture (a simple model of electrolytes beyond the primitive model). It should be mentioned here that for this model an *analytical* solution within the ‘mean-spherical approximation’ (MSA) [7, 8] is available for the fully symmetric (equal-sized hard-spheres) case. In this contribution we go one step further and present results obtained from a *numerical* treatment of the OZ-type equations, complemented by the linear SSCA/EMA closure relation. Recently, we have reported the implementation of an algorithm to solve this problem and given results for a rather *academic* model of Hg [9].

While this paper was devoted to a presentation of the specific formalism and the numerical solution algorithm, the present contribution deals with its application to a more realistic problem, namely the determination of the electronic structure of liquid silicon.

As outlined in more detail by Virkkunen *et al* [10], ‘the proper physical description of the properties of liquid silicon is a great challenge and also of substantial practical interest’. The atomic and electronic structure of liquid silicon have been studied before using different methods, such as *ab initio* simulations [11–13] or TB molecular-dynamics (TB-MD) simulations [10, 14, 15]. In a TB-MD simulation, the atomic and electronic structures are determined simultaneously, the contribution to the atomic forces due to the band-structure energy being calculated via the Hellmann–Feynman theorem. For silicon, a very successful TB parametrization has been proposed by Goodwin *et al* [16] (based, in turn, on a parametrization by Harrison [17]). In the present paper, we use our integral-equation approach to determine the electronic structure; in order to check the reliability and accuracy of our results we have also performed TB-MD simulations, using a 256-particle sample.

Comparison of the integral-equation results and the simulation data shows very satisfactory agreement. Since the TB-MD method is known to compare well to *ab initio* simulations, we can conclude that this integral-equation approach represents a powerful and reliable complement to *ab initio* [11, 12, 18] simulations in determining the electronic structure of disordered materials. As to the atomic structure, the approach presented herein relies on external input, and unlike the simulation it cannot be determined within this treatment. This limitation might in principle be overcome by an extension of the self-consistent procedure that has already proven efficient in simple one-band fluids [19].

The paper is organized as follows: in the next section we briefly present the integral-equation approach (leaving, however, technical details to the previous contribution [9]), and we specify the TB model used for liquid Si and give some details about the TB-MD simulation. In section 3 we discuss the results and the paper is closed with concluding remarks and prospects for the future.

2. Theory

2.1. The integral-equation approach

In our approach we consider a disordered medium which is described by a ‘tight-binding’ (TB) Hamiltonian of the form

$$H = \sum_{i;\alpha} \varepsilon_i^\alpha a_{i\alpha}^\dagger a_{i\alpha} + \sum_{i \neq j; \alpha, \beta} V^{\alpha\beta}(\mathbf{r}_{ij}) a_{i\alpha}^\dagger a_{j\beta}. \quad (1)$$

i and j characterize the sites and α, β describe the electronic levels (s and p basis functions) located on each site and the $V^{\alpha\beta}(\mathbf{r}_{ij})$ are the transfer-matrix elements (TME). In this study we will restrict ourselves to off-diagonal disorder, and hence $\varepsilon_i^\alpha = \varepsilon_\alpha$. We have furthermore considered a two-centre approximation, i.e., we have neglected crystal-field and three-centre integrals, as well as the non-orthogonality of the basis-functions. Under these conditions the above Hamiltonian can be split into intra- and interatomic components

$$H = \sum_{i \neq j} H_{ij} + \sum_i H_{ii}. \quad (2)$$

Following Slater and Koster [20], these terms can be rewritten—and using the notation of [9]—as

$$H_{ii} = \varepsilon_s a_{is}^\dagger a_{is} + \varepsilon_p \sum_{\mu=x,y,z} a_{ip\mu}^\dagger a_{ip\mu} \quad (3)$$

$$H_{ij} = V^{ss}(r_{ij})a_{is}^\dagger a_{js} + V_\sigma^{sp}(r_{ij})a_{is}^\dagger \mathbf{a}_{jp} \cdot \hat{\mathbf{r}}_{ij} + V_\sigma^{ps}(r_{ij})\hat{\mathbf{r}}_{ij} \cdot \mathbf{a}_{ip} a_{js}^\dagger + V_\pi^{pp}(r_{ij})(\mathbf{a}_{ip}^\dagger \cdot \mathbf{a}_{jp}) + [V_\sigma^{pp}(r_{ij}) - V_\pi^{pp}(r_{ij})](\mathbf{a}_{ip}^\dagger \cdot \hat{\mathbf{r}}_{ij})(\hat{\mathbf{r}}_{ij} \cdot \mathbf{a}_{jp}) \quad (4)$$

with

$$\hat{\mathbf{r}}_{ij} = \mathbf{r}_{ij}/|\mathbf{r}_{ij}|. \quad (5)$$

We are now interested in the ensemble-averaged off-diagonal (diagonal) Green-function $\bar{G}^{\alpha\beta}(\mathbf{r}_{12}, z)$ ($\bar{G}^{\alpha\beta}(z)$). It can be shown [1, 9] that the following equation can be deduced:

$$z_\alpha \bar{G}^{\alpha\beta}(z) = \delta_{\alpha\beta} + \rho \sum_\gamma \int d\mathbf{r}_2 V^{\alpha\gamma}(\mathbf{r}_{12}) \bar{G}^{\gamma\beta}(\mathbf{r}_{21}, z) \quad (6)$$

where ρ is the number density of the system.

Using graph-theoretical methods one may show that the off-diagonal Green function can be expressed as [1, 21]

$$\bar{G}^{\alpha\beta}(\mathbf{r}_{12}, z) = \sum_{\gamma\delta} \bar{G}^{\alpha\gamma}(z) H^{\gamma\delta}(\mathbf{r}_{12}) \bar{G}^{\delta\beta}(z) \quad (7)$$

where the spatial dependence is now transferred to the function $H^{\alpha\beta}(\mathbf{r}_{12})$. This function, in turn, can be split into sets of diagrams with and without bridge points [1, 3], thus defining functions $C^{\gamma\delta}(\mathbf{r}_{12})$ that correspond to the direct correlation function in liquid-state physics; $C^{\gamma\delta}(\mathbf{r}_{12})$ and $H^{\gamma\delta}(\mathbf{r}_{12})$ are thus linked by an OZ-type equation:

$$H^{\alpha\beta}(\mathbf{r}_{12}) = C^{\alpha\beta}(\mathbf{r}_{12}) + \rho \sum_{\gamma\delta} \int d\mathbf{r}_3 H^{\alpha\gamma}(\mathbf{r}_{13}) \bar{G}^{\gamma\delta}(z) C^{\delta\beta}(\mathbf{r}_{32}). \quad (8)$$

It should be noted that neither $H^{\alpha\beta}(\mathbf{r}_{12})$ nor $C^{\alpha\beta}(\mathbf{r}_{12})$ are spherically symmetric.

Eliminating the off-diagonal Green function in (6) by means of (7) we obtain (using the compact matrix formulation introduced in [9]) the additional relation

$$z\bar{\mathbf{G}}(z) = \mathbf{I} + \rho \int d\mathbf{r}_2 \mathbf{V}(\mathbf{r}_{12}) \bar{\mathbf{G}}(z) \mathbf{H}(\mathbf{r}_{21}) \bar{\mathbf{G}}(z) \quad (9)$$

where \mathbf{I} stands for the unit matrix. The OZ-type equations (8) have to be supplemented by a closure relation; in this contribution we have used the linear SSCA/EMA closure, i.e.,

$$C^{\alpha\beta}(\mathbf{r}_{12}) = g(\mathbf{r}_{12}) V^{\alpha\beta}(\mathbf{r}_{12}) + [g(\mathbf{r}_{12}) - 1][H^{\alpha\beta}(\mathbf{r}_{12}) - C^{\alpha\beta}(\mathbf{r}_{12})]. \quad (10)$$

$g(r)$ is the PDF characterizing the structure of the disordered medium.

In the SSCA/EMA approximate theory (though not in the general theory of [1]) the structure of the disordered medium is represented at the level of two-particle correlations, namely the PDF $g(r)$. In the present calculation, the PDF was taken from the TBMD simulation (see below) which incorporates the many-body Hellmann–Feynman forces appropriate to liquid Si. After some manipulation it becomes obvious that the problem of solving equation (8) is now formally equivalent to the solution of the OZ equation for an ion–dipole mixture of liquid-state physics. Drawing on parallels developed for this problem [22] we can obtain a numerical solution of this complex-valued OZ-type equation (for details we refer the reader to [9]).

Once we have solved these equations we obtain the DOS $D(E)$ via

$$D(E) = - \lim_{\epsilon \rightarrow 0^+} \frac{1}{\pi} [\bar{G}^{ss}(E + i\epsilon) + 3\bar{G}^{pp}(E + i\epsilon)]. \quad (11)$$

2.2. The parametrization for silicon

In the present work we have used the empirical TB Hamiltonian proposed by Goodwin *et al* [16] for silicon, which, in turn, is based on a model proposed by Harrison [17], rescaling the TMEs by a smoothed step function:

$$\begin{aligned}
 V^{ss}(r) &= V^{ss}(r_0) f(r) \\
 V_{\sigma}^{pp}(r) &= V_{\sigma}^{pp}(r_0) f(r) \\
 V_{\pi}^{pp}(r) &= V_{\pi}^{pp}(r_0) f(r) \\
 V_{\sigma}^{sp}(r) &= V_{\sigma}^{sp}(r_0) f(r) \\
 V_{\sigma}^{ps}(r) &= -V_{\sigma}^{sp}(r)
 \end{aligned} \tag{12}$$

with

$$f(r) = \left(\frac{r_0}{r}\right)^2 \exp\left\{2\left[-\left(\frac{r}{r_c}\right)^{n_c} + \left(\frac{r_0}{r_c}\right)^{n_c}\right]\right\}. \tag{13}$$

The numerical parameters of this parameterization were taken from Virkkunen *et al* [10]:

$$\begin{aligned}
 V^{ss}(r_0) &= -1.820 \text{ eV} & V_{\sigma}^{sp}(r_0) &= 1.960 \text{ eV} \\
 V_{\sigma}^{pp}(r_0) &= 3.060 \text{ eV} & V_{\pi}^{pp}(r_0) &= -0.870 \text{ eV} \\
 \varepsilon_s &= -6.173 \text{ eV} & \varepsilon_p &= 2.122 \text{ eV} \\
 r_c &= 3.6 \text{ \AA} & n_c &= 6.48.
 \end{aligned} \tag{14}$$

$r_0 = 2.35 \text{ \AA}$ is the equilibrium nearest-neighbour distance of the diamond lattice.

The repulsive energy U_{rep} is constructed from a sum of two-centre potentials:

$$U_{\text{rep}} = \sum_{i,j:i \neq j} \Phi(r_{ij}) \tag{15}$$

where the following expression has been used for $\Phi(r)$:

$$\Phi(r) = \Phi(r_0) \left(\frac{r_0}{r}\right)^{4.54} \exp\left\{4.54\left[-\left(\frac{r}{r_c}\right)^{n_c} + \left(\frac{r_0}{r_c}\right)^{n_c}\right]\right\}. \tag{16}$$

$\Phi(r_0) = 3.4581 \text{ eV}$, and r_c and n_c are given in (14).

In this contribution silicon was studied at a temperature of 1740 K and a mass density of 2590 kg m^{-3} , i.e., at a state close to the triple point.

2.3. The ‘tight-binding’ molecular-dynamics simulation

The TB-MD simulation is based on a classical standard MD simulation for a system of N particles. The forces acting on the particles are put together on the one hand from the forces resulting from the repulsive energy (15) and on the other hand from the Hellmann–Feynman forces (see, e.g., [23]), which—as the most time-consuming part of the simulation—are obtained by an exact diagonalization of the $4N \times 4N$ Hamilton matrix, built up by the TMEs $V^{\alpha\beta}(\mathbf{r}_{ij})$.

Introducing periodic boundary conditions makes the diagonalization of the Hamilton matrix in q -space more convenient [24]. Little is known on the dependence of these results on the choice of the q -vectors for a *finite* number of particles N in the simulation cell (for $N \rightarrow \infty$ the results should be independent of q). In the present work we found that even just one q -vector (i.e., the Γ point) turns out to be sufficient.

The eigenvalues of the Hamilton matrix determined in this way, and averaged over a sufficient number of atomic configurations, yield the DOS results of the simulation. In practice, the Hellmann–Feynman forces have been calculated in every time step Δt , while the determination of the DOS was done every $10 \Delta t$.

Starting from an fcc lattice of 256 particles the system was melted at a temperature of 2700 K and was then cooled down to the desired temperature of 1740 K. After equilibration at this temperature the production job extended over 5000 Δt with $\Delta t = 1$ fs.

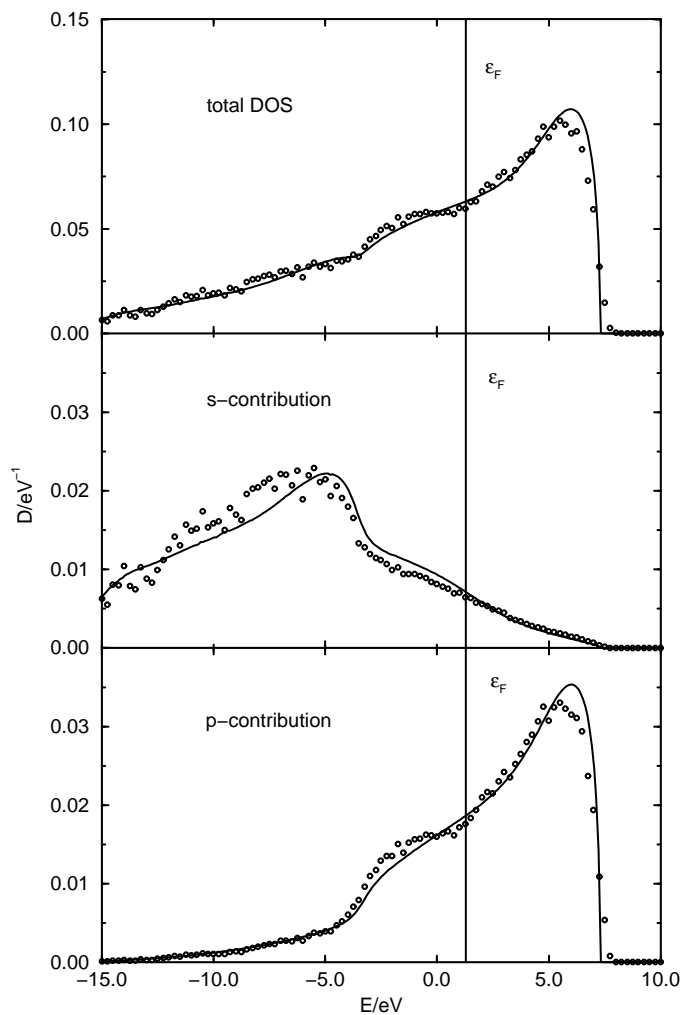


Figure 1. Total (top) and partial (middle; s contribution; bottom: single-orbital p contribution) DOS as obtained from the integral-equation approach (full lines) and the TB-MD simulation (\circ).

3. Results

In figure 1 we compare the results for the DOS obtained in the integral-equation approach with data calculated in the TB-MD simulation; we display both the total DOS as well as the

partial s and p contributions. The DOS terminates at high energies because of the limited basis set employed. The Fermi energy however lies well within the band, confirming that liquid Si is metallic. Agreement is very satisfactory and thus proves the reliability of the integral-equation approach. Comparing the required CPU time for the two methods we find that the latter is at least two orders of magnitude faster; this should encourage future applications of the integral-equation approach to similar problems. The CPU time required by the TB-MD simulation depends of course on the size of the simulation cell employed; in contrast, the integral-equation results are, by construct, for an infinite system.

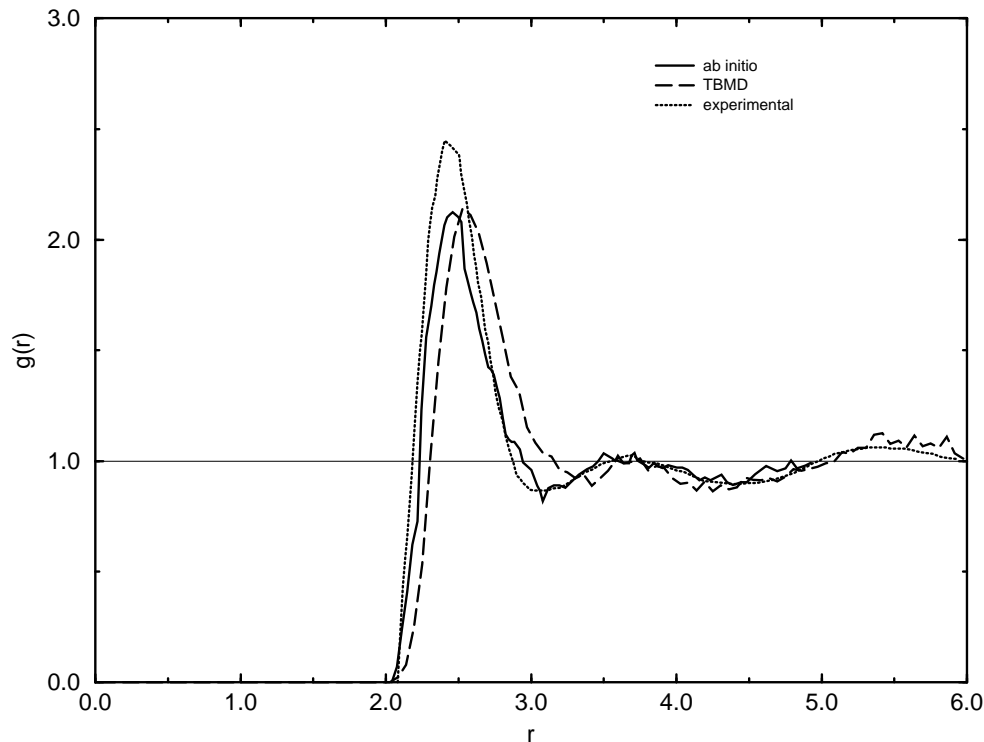


Figure 2. The PDF for liquid Si as obtained from the present study and from *ab initio* simulations in comparison with experimental scattering data [13, 25]; for the interpretation of the curves, see the key. r is in units of Å.

The PDF as obtained from the TB-MD simulation (figure 2) is in reasonable agreement with other theoretical studies [15, 12, 13] and with experimental neutron-scattering data [25] (quoted in [13]); differences have to be attributed to size effects. On the other hand it should be pointed out that a ‘better’ PDF obtained for instance from a larger sample would modify the integral-equation results for the DOS only marginally, since the DOS is rather insensitive to small changes in the structure.

4. Conclusion and outlook

We have shown that an integral-equation approach for calculating the electronic DOS of a liquid is able to give reliable and accurate results which compare well with TB-MD simulation data. Future work in this field will be devoted to the following topics.

(i) In order to describe the atomic and electronic structure of a liquid *self-consistently* we plan (as outlined for the one-band case in [19]) to integrate this integral-equation approach into an iterative procedure: starting, e.g., from the repulsive potential energy U_{rep} we construct via some integral-equation method the atomic structure of the system in terms of the PDF; this information is fed into the closure relation and the electronic DOS is calculated as outlined in this contribution. From the electronic structure we calculate the corresponding contribution to an effective pair potential (the exact contribution is a many-body one), which yields a new effective interaction. For this potential the atomic structure is calculated again; the procedure is iterated until self-consistency is achieved, i.e., until the interactions of two subsequent steps coincide in the numerical sense. Previous results for the one-band case have shown that convergence is rather fast.

(ii) It is well known [26, 27] that the linear closure used in the present contribution leads to less reliable results in the low-density regime. This is however less relevant for the densities of interest when considering liquids and amorphous materials, except for the high-energy wings of the spectra that are typically missing in linear approximations, and that in other problems might be quite important [9, 27]. In this connection, a non-linear correction along the lines devised in [27] is currently under investigation for sp^3 TB models.

Concluding, we think that this method, along with the two amendements mentioned above, would represent an attractive and less time-consuming complement to TB-MD or even *ab initio* simulations.

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