

A NOVEL APPROACH TO FORCE AND STANDARD BAND-STRUCTURE CALCULATIONS

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A unified approach to the density functional theory and molecular dynamics is reviewed. Starting from the molecular dynamics equations the standard electronic structure problem is reformulated and a new method based on the conjugate gradient strategy is introduced. Finally, the unified approach is used in a first-principles study of short-range order and bonding in metallic liquid Silicon.

I. INTRODUCTION

It has always been a dream of condensed-matter physicists to predict properties of the matter such as atomic structure, chemical bonding, dynamical and transport properties. It is a great challenge to cope with this problem by a rigorous quantum-mechanical calculation of many-body interatomic potentials, which automatically conveys information on structural stability, chemical bonding and more generally is a basis to calculate many-body forces to study dynamical and transport properties. Although old in principle, the lack of computational possibilities and new ideas have until recently precluded a practical use of this idea.

On the other hand, the well-known Density Functional Theory (DFT) [1] provides a very satisfactory description of interatomic potentials and chemical bonding, whereas the Molecular Dynamics method (MD) [2] is successful in predicting both equilibrium and non-equilibrium properties of condensed systems. Thus it is a natural idea to connect them. However, this is not easy because the DFT is computationally so intensive that its straightforward application to calculate forces for MD was not manageable.

Recently, new theoretical methods have appeared that overcome the above mentioned difficulties and allow for a unified approach to MD and DFT [3]. The method became known as the 'Car-Parinello method' (CP). CP is physically

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very appealing because it not only allows for an 'ab-initio' MD and finite temperature studies of condensed matter (including thermal treatments and simulated annealing [4]) but it also recasts the standard electronic structure problem in a very lucid and convenient way.

The paper is organized as follows. In Sect. II the basic notation is introduced and a brief summary of the main concepts of the CP is given. Sect. III is devoted to the application of the CP method to the standard electronic structure problem. In particular, we present a convenient new method for the solution of the electronic structure problem. Sect. IV deals with the application of the 'ab-initio' MD to non-simple liquid metals. As an example we present our results on the simulation of liquid Silicon (1-Si) by CP. Finally, Sect. V contains our conclusions.

II. AN ALTERNATIVE TO CALCULATE MANY-BODY FORCES

We summarize here the basic idea of the CP method and compare it with more traditional approaches. Let us start from the Born-Oppenheimer approximation (BO) and the assumption that the ionic motion follows the classical mechanics. The corresponding point on the BO surface for each ionic configuration $\{\mathbf{R}_I\}$ (ground-state energy), $\phi[\{\mathbf{R}_I\}]$, is defined as the minimum of the functional $E[\{\psi\}, \{\mathbf{R}_I\}]$ with respect to 'electronic degrees of freedom' $\{\psi\}$, i.e.

$$\phi[\{\mathbf{R}_I\}] = \min_{\{\psi\}} E[\{\psi\}, \{\mathbf{R}_I\}]. \quad (1)$$

We follow here the DFT [1], where

$$E[\{\psi\}, \{\mathbf{R}_I\}] = \sum_i^{\text{occ}} \int d\mathbf{r} \psi_i^*(\mathbf{r}) \left(-\frac{1}{2} \nabla^2 \right) \psi_i(\mathbf{r}) + \int d\mathbf{r} V^{\text{ext}}(\mathbf{r}) n(\mathbf{r}) + \\ + \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E^{\text{xc}}[n] + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} \quad (2)$$

and the principal quantity, the ground-state electronic density $n(\mathbf{r})$, can be expressed in terms of N occupied single-particle orbitals as

$$n(\mathbf{r}) = \sum_i^{\text{occ}} |\psi_i(\mathbf{r})|^2. \quad (3)$$

The atomic units $e = \hbar = m_e = 1$ are used throughout the paper. In eq. (2) $E^{\text{xc}}[n]$ is the exchange-correlation energy [1], V^{ext} is the total external potential felt by the electrons, and Z_I are the charges of ionic cores. The single-particle orbitals $\{\psi_i\}$ are subjected to orthonormality constraints:

$$\int d\mathbf{r} \psi^*(\mathbf{r}) \psi_j(\mathbf{r}) = \delta_{ij}. \quad (4)$$

Quite a lot of information can be obtained from studies of total energies (eqs. 1–4) but force calculations and moving nuclei in response to the forces convey more information.

The many-body force \mathbf{F}_I acting on the ion I can be defined close to the ground-state as

$$\mathbf{F}_I = -\nabla_{\mathbf{R}_I} E[\{\psi_j\}, \{\mathbf{R}_j\}] = F_I^{HF} - 2\mathcal{Q} \sum_j^{\text{occ}} \int d\mathbf{r} \frac{\partial \psi_j^*}{\partial \mathbf{R}_I} \left[-\frac{1}{2} \nabla^2 + V^{\text{ext}}(\mathbf{r}) + \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta E^{\text{xc}}[n]}{\delta n(\mathbf{r})} - \epsilon_j \right] \psi_j = F_I^{HF} - 2\mathcal{Q} \sum_j^{\text{occ}} \int d\mathbf{r} \frac{\partial \psi_j^*}{\partial \mathbf{R}_I} [H^{DFT} - \epsilon_j] \psi_j, \quad (5a)$$

where $F_I^{HF} = \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J (\mathbf{R}_I - \mathbf{R}_J)}{|\mathbf{R}_I - \mathbf{R}_J|^3} - \int d\mathbf{r} \frac{\partial V^{\text{ext}}(\mathbf{r})}{\partial \mathbf{R}_I} n(\mathbf{r})$ is the Hellmann-Feynman (HF) [5] force equal to the classical force arising from all charged ions and the electronic charge density calculated quantum-mechanically, and ϵ_j is the Lagrange multiplier imposing the orthonormality constraint (eq. (4)). Introducing the finite precision in the electronic minimization in eq. 1 ($H^{DFT} \rightarrow \tilde{H}^{DFT}$), eq. (5a) can be recast in the following form

$$\mathbf{F}_I = F_I^{HF} - 2\mathcal{Q} \sum_j^{\text{occ}} \int d\mathbf{r} \frac{\partial \psi_j^*}{\partial \mathbf{R}_I} [\tilde{H}^{DFT} - \epsilon_j] \psi_j - \int d\mathbf{r} \frac{\partial n(\mathbf{r})}{\partial \mathbf{R}_I} [H^{DFT} - \tilde{H}^{DFT}]. \quad (5b)$$

The first correction to the HF force is known as the Pulay force [6], whereas the second term arises due to imperfect minimization of the functional in eq. (2). Clearly, if $\{\psi_j\}$ are expanded in a basis set that doesn't make any reference to $\{\mathbf{R}_j\}$, then the Pulay force vanishes.

For that reason we limit our discussion to the single-particle orbitals expanded into plane waves [7]

$$\psi_j(\mathbf{r}) = \sum_{\mathbf{g}} c_{\mathbf{g}}^j e^{i(\mathbf{g} \cdot \mathbf{r})} \quad (6)$$

with the sum truncated to include only M plane waves.

The conventional approach now proceeds as follows. Atomic coordinates are chosen. For that configuration the self-consistent charge density is calculated by solving the Kohn-Sham (KS) equations [8]

$$H^{DFT} \psi_j(\mathbf{r}) = \epsilon_j \psi_j(\mathbf{r}) \quad (7)$$

(typically by some sort of matrix diagonalization technique — for more details cf. Sect. III). Using that density in formulae (5) allows to calculate forces acting on ions. Then the ionic positions are updated and the self-consistent calculation

repeated. The calculation of the charge density by matrix diagonalization requires $O(M^3)$ operations that must be repeated L_{sc} times to iterate the density to self-consistency. Clearly, this procedure is inefficient because it generates all the M eigenstates, whereas only the occupied N orbitals are really necessary to calculate the forces.

Let us now outline how the above difficulties can be avoided within CP and the self-consistency and structure determination achieved simultaneously. The MD method may be invoked by setting up a quantum-classical system defined by the Lagrangian [3]

$$L = \sum_j^I \frac{1}{2} \mu \dot{\mathbf{r}}_j^2 + \sum_j^I \frac{1}{2} M_j \dot{\mathbf{R}}_j^2 - E[\{\psi_j\}, \{\mathbf{R}_j\}] + \sum_j^I \Lambda_j \int d\mathbf{r} (\psi_j^* \psi_j - \delta_{ij}). \quad (8)$$

In eq. (8) the dot indicates the time derivative, μ is the fictitious mass of the single-particle orbitals to define the fake kinetic energy of the wavefunctions, M_j are the physical ionic masses, and Λ is the hermitian matrix of Lagrange multipliers imposing the orthonormality constraints from eq. (4).

The lagrangian in eq. (8) generates the following fictitious dynamics for the electronic orbitals

$$\mu \ddot{\psi}_j(\mathbf{r}, t) = -\frac{\delta E}{\delta \psi_j^*(\mathbf{r}, t)} + \sum_j^I \Lambda_j \psi_j(\mathbf{r}, t) = -H^{DFT} \psi_j(\mathbf{r}, t) + \sum_j^I \Lambda_j \psi_j(\mathbf{r}, t) \quad (9a)$$

and the real dynamics for the ionic position

$$M_I \ddot{\mathbf{R}}_I = -\nabla_{\mathbf{R}_I} E. \quad (9b)$$

The force in eqs. (9a) acting on the electronic orbitals is of two different kinds: the force from the Hamiltonian and the force of constraint. Since we want eqs. (9b) to generate the B0 trajectories some additional conditions have to be satisfied:

- The system must initially be prepared in the ground-state.
- The electronic dynamics must proceed fast in order that the electronic orbitals have always time to catch up their delay with respect to the ionic positions, i.e. the dynamics must be adiabatic with no energy transfer between electronic and ionic subsystems. This, in turn, means that $\mu \ll M_I$. Only then eq. (1) will be approximately satisfied. The important point is that the electronic optimization proceeds dynamically, following second-order differential equations.

Classical kinetic energy can be ascribed to the system

$$K = \sum_j^I \frac{1}{2} \mu \dot{\mathbf{r}}_j^2 + \sum_j^I \frac{1}{2} M_j \dot{\mathbf{R}}_j^2 \quad (10)$$

and its temporal average is related to the system temperature T . Thus simulated annealing can be carried out with the system and for $T \rightarrow 0$ the equilibrium state with a minimal E with respect to both $\{\psi_i\}$ and $\{R_i\}$ can eventually be reached. Thus diagonalization, self-consistency, and ionic relaxation are achieved simultaneously and on the same footing. Moreover, eqs. (9) constitute an 'ab-initio' form of MD.

The CP does not generate any redundancy in the information since it involves only the N occupied orbitals. The kinetic energy is diagonal in the Fourier space, whereas the potential energy is diagonal in the real space. Thus if Fast Fourier Techniques (FFT) are used to calculate $H * \psi$ always in the 'easy space', it requires $O(NM \ln M)$ operations, and additional $O(N^2 M)$ operations are required to impose the orthonormality constraints. Since usually $N \ll M$ this compares very well with the direct approach requiring $O(M^3)$ operations.

III. ELECTRONIC STRUCTURE BY DIRECT MINIMIZATION OF THE ENERGY FUNCTIONAL

In this section the standard electronic structure problem is rewritten in the language introduced in Sect. II. In particular, we introduce and test a new effective iterative method as an alternative to solving the KS equations.

The objective now is to solve eq. (1) for fixed $\{R_i\}$. One can directly start from eqs. (9a) and perform simulated annealing by reducing the system temperature defined through eq. (10), $T \rightarrow 0$. In equilibrium $\{\psi_i = 0\}$, and it is easily verified that eqs. (9a) are then identical (within unitary transformation) to the KS equations.

It has formally always been part of the theory to carry out the minimization indicated in eq. (1), but it has until recently never been used in a practical way. The standard way of solving eq. (1) subject to the constraints of eq. (4) consists in solving the associated Euler-Lagrange equations

$$H\psi_i(r) = \epsilon_i \psi_i(r) \quad (10)$$

$$\left\{ -\frac{1}{2} \nabla^2 + V^{ext}(r) + V^H(r) + \mu^x(r) \right\} \psi_i(r) = \epsilon_i \psi_i(r), \quad (11)$$

where $V^H(r) = \int d r' \frac{n(r')}{|r - r'|}$ is the Hartree potential and $\mu^x(r) = \frac{\delta E^x[n]}{\delta n(r)}$ is the exchange-correlation potential. The Schrödinger-type eqs. (11) are called the Kohn-Sham equations. In the plane wave formalism, using eq. (6) in eq. (11) yields for any \mathbf{k} vector from the Brillouin zone (BZ) the following equation

$$\sum_{\mathbf{G}} H_{\mathbf{G}\mathbf{G}'} c_{\mathbf{G}}^{n\mathbf{k}} = \epsilon^{n\mathbf{k}} c_{\mathbf{G}}^{n\mathbf{k}} \quad (12)$$

with the Hamiltonian matrix

$$H_{\mathbf{G}\mathbf{G}'}^{n\mathbf{k}} = \frac{1}{2} |\mathbf{k} + \mathbf{G}|^2 \delta_{\mathbf{G}\mathbf{G}'} + V_{\mathbf{G}-\mathbf{G}'}^H + V_{\mathbf{k}+\mathbf{G}, \mathbf{k}+\mathbf{G}'}^{ext} + \mu_{\mathbf{G}-\mathbf{G}'}^x \quad (13)$$

The straightforward diagonalization of the matrix $H_{\mathbf{G}\mathbf{G}'}^{n\mathbf{k}}$ requires $O(M^3)$ operations. If instead eqs. (9a) are used, the cost of a single step in the limit of a large system is $O(N^2 M)$ [9], as explained in Sect. II. This represents a substantial saving in a single MD step compared to the straightforward diagonalization, but usually the number of self-consistent iterations I_{sc} in the MD method is larger. Hence, in this form both methods may be of comparable efficiency. Thus the key point is to reduce I_{sc} to a more manageable value.

Technically, the above method is merely a refinement to expedite the convergence in a self-consistent calculation by replacing the diagonalization techniques by FFT techniques. But it is probably more than this, since it reformulates the standard band-structure problem in an original form of great clarity and simplicity.

The main aim in reducing I_{sc} is that if the ions are kept fixed only a single minimum is encountered [10]. In this case the efficiency improves if MD is substituted by a method allowing only for downhill moves. The simplest way to do it is provided by the Steepest Descent method (SD) which can be formulated in terms of the equations

$$\dot{\psi}_i(r, t) = -\frac{\delta E}{\delta \psi_i^*(r, t)} + \text{constraints}. \quad (14)$$

The 'time' dependence in eqs. (14) is fictitious since in SD only the final result is important. Here the time is used to label configurations in the $\{\psi_i\}$ space. The $\{\psi_i(t=0)\}$ is the initial trial state that has to be non-orthogonal to the final state. The efficiency of SD is controlled by the number of steps necessary to achieve convergence. This can be large in low symmetry situations or even for a quadratic canyon-like function [11].

This drawback can be eliminated by using the information on the matrix of second derivatives A of the function f to be minimized. However, the calculation of the Hessian matrix A in the space of expansion coefficients of the wavefunctions cannot be carried out explicitly. Thus we need a method that avoids the explicit calculation of A . Such a possibility is provided by the Conjugate Gradient method (CG) [11]. It defines an iterative minimization procedure

$$p^{(n+1)} = p^{(n)} + \lambda^{(n)} \mu^{(n)}, \quad n = 0, 1, 2, \dots, \quad (15)$$

where $\lambda^{(n)}$ is a scalar and $\mu^{(n)}$ is a vector in multidimensional space. In the CG method information on A is only used implicitly to define an optimal set of directions $\mu^{(n)}$ in the sequence (15), where the scalar $\lambda^{(n)}$ is obtained by a

one-dimensional minimization along the line defined by $\mu^{(n)}$. The directions $\mu^{(n)}$ are given by:

$$\mu^{(n)} = \begin{cases} \mathbf{g}^{(n)}, & n = 0 \\ \mathbf{g}^{(n)} + \gamma^{(n-1)}\mu^{(n-1)}, & n = 1, 2, 3 \dots \end{cases} \quad (16)$$

with

$$\begin{aligned} \mathbf{g}^{(n)} &= -\nabla f(\mathbf{P}^{(n)}) \\ \gamma^{(n)} &= \frac{\langle \mathbf{g}^{(n+1)} | \mathbf{g}^{(n+1)} \rangle}{\langle \mathbf{g}^{(n)} | \mathbf{g}^{(n)} \rangle}. \end{aligned} \quad (17)$$

The directions $\mu^{(n)}$ are said to be conjugate and for a quadratic function the following conjugacy property is fulfilled

$$\langle \mu^{(n)} | A | \mu^{(m)} \rangle = 0, \quad \forall n \neq m. \quad (18)$$

This property guarantees that a successive step is always an improvement on the preceding ones.

We want to apply this standard theory to a constrained problem of the electronic structure [12]. It means that the forces of constraint have to be taken into account when the line minimizations are carried out. It is convenient to reformulate the problem in terms of linearly independent but not orthonormal orbitals $\{\varphi_j\}$. The orthonormal orbitals $\{\psi_j\}$ are related to the $\{\varphi_j\}$ via

$$\psi_j = \sum_i S_{ij}^{-1/2} \varphi_i, \quad (19)$$

with

$$S_{ij} = \langle \varphi_j | \varphi_i \rangle \quad (20)$$

being the overlap matrix. In terms of the $\{\varphi_j\}$ the particle density $n(\mathbf{r})$ is given by:

$$n(\mathbf{r}) = \sum_j^{\text{occ}} \psi_j^*(\mathbf{r}) \psi_j(\mathbf{r}) = \sum_{ij}^{\text{occ}} S_{ij}^{-1/2} \varphi_i^*(\mathbf{r}) S_{ij}^{-1/2} \varphi_j(\mathbf{r}) = \sum_{ij}^{\text{occ}} \varphi_i^*(\mathbf{r}) S_{ij}^{-1} \varphi_j(\mathbf{r}) \quad (21)$$

and the functional E in eq. (2) to be minimized can be written as

$$\begin{aligned} E &= \sum_{ij}^{\text{occ}} S_{ij}^{-1} \left\langle \varphi_i - \frac{1}{2} \nabla^2 \varphi_j \right\rangle + \int d\mathbf{r} V^{\text{ext}}(\mathbf{r}) n(\mathbf{r}) + \\ &+ \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E^{\text{xc}}[n] + \frac{1}{2} \sum_{i \neq j} \frac{Z_i Z_j}{|\mathbf{R}_i - \mathbf{R}_j|}. \end{aligned} \quad (22)$$

The constrained functional derivative of E with respect to the $\{\varphi_j\}$ is given by

$$\frac{\delta E}{\delta \varphi_j^*(\mathbf{r})} = \sum_{ij} S_{ij}^{-1} H \varphi_j(\mathbf{r}) - \sum_{im} \langle \varphi_i | H | \varphi_j \rangle S_{im}^{-1} S_{ij}^{-1} \varphi_m(\mathbf{r}). \quad (23)$$

Although in principle irrelevant, it is convenient to reorthonormalize $\{\varphi_j\}$ at each step. Then eqs. (23) reduces to

$$\frac{\delta E}{\delta \varphi_j^*(\mathbf{r})} = H \varphi_j(\mathbf{r}) - \sum_m \langle \varphi_m | H | \varphi_j \rangle \varphi_m(\mathbf{r}). \quad (24)$$

Eqs. (24) define the functional derivative $\mathbf{g}^{(n)}$ in the CG procedure in eqs. (16, 17) and complete the necessary prerequisites. In order to keep things simpler, we introduce in the numerical example below an additional approximation and in the one-dimensional minimizations we proceed as in a non self-consistent case and keep V^H and μ^{xc} constant as $\lambda^{(n)}$ varies.

We have performed a number of tests to study the efficiency of various methods for electronic structure calculations. In particular, we compare our CG based strategy with SD and with a more traditional and well-known Davidson iterative method (DI) [13]. DI is a prototype of methods where only a partial diagonalization yielding only the lowest energy eigenstates is carried out. We use the non-local norm-conserving pseudopotentials [14]. The exchange-correlation effects are treated in the Local Density Approximation (LDA) [1] in the parameterization of ref. [15]. The Gram-Schmidt procedure was used to reorthonormalize the wavefunctions at each step.

As a representative result we consider here a calculation based on a periodically repeated simple cubic supercell with the lattice constant $a = 10.26$ a.u. with eight Silicon atoms that were randomly displaced from their perfect diamond positions with a maximum amplitude of 0.2 a.u. The energy cutoff of 7 Ry was used in a plane wave calculation. The Brillouin zone integral was approximated by the $\mathbf{k} = \left(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\right)$ point [16]. The initial trial state was obtained by filling the

lowest energy states generated by a diagonalization of a small Hamiltonian matrix constructed from a uniform valence density and an energy cutoff of 2 Ry.

The efficiency of different schemes measured in the number of steps necessary to achieve convergence in the total energy is given in Tab. and Fig. 1. We remark that for this system size the operations of the type $H * \psi$ dominate and the approximate cost of the CG step is equal to the DI step and twice the SD step. In the limit of a very large system size the CG step is slightly more economical than the DI step. We see that both DI and CG have a much faster rate of convergence than SD but CG is significantly better than DI. The CG method moreover does not require any convergence controlling parameter, such as the

Table 1

	SD	DI	CG
$\text{Si} \left(\mathbf{k} = \begin{pmatrix} 1 & 1 & 1 \\ 4 & 4 & 4 \end{pmatrix} \right)$	73	26(6)	16

Comparison of SD, DI, and CG methods in number of steps for the Silicon system. Convergence in seven significant figures is assumed. The timestep $\Delta = 0.16$ in the SD method. For the DI method, the number of self-consistency cycles L_{sc} is given in parenthesis.

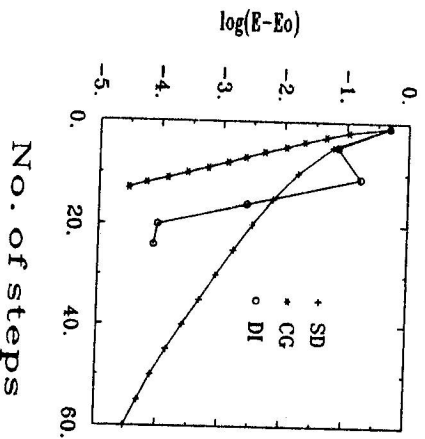


Fig. 1 The rate of convergence of the total energy E in SD, DI, and CG methods for the Silicon system. E_0 stands for the ground-state energy.

time step Δ in SD or the mixing parameter between input and output potentials in DI. There is now much interest in large-scale DFT calculations in the LDA approximation [17]. We think that our CG based strategy is a suitable candidate for that type of calculations.

IV. 'AB-INITIO' MOLECULAR DYNAMICS AN APPLICATION TO A NON-SIMPLE LIQUID METAL

In this section we will discuss the application of eqs. (9) to generate the finite temperature dynamics of a non-simple liquid metal — liquid Silicon. In Sect. III an efficient approach to the standard electronic structure problem was developed. However, when ions are moving the dynamical optimization of electronic degrees of freedom (eqs. (9a)) is always more efficient than the combination of eqs. (9b) with any electronic optimization based on first-order differential equations.

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Unlike with semiconductors or insulators, there are a number of complications caused by the fact that we deal with a metal. So far there has been no successful application of CP to a metallic system. Let us only briefly comment on some of the difficulties.

In a metal there are degenerate states at the Fermi level. Those states should be occupied by non-fixed fractional occupation numbers (at high temperature we should also use the finite temperature version of DFT and minimize the Mermin [18] rather than the KS functional). The special points sampling of the BZ is not directly applicable here because the function to be sampled is discontinuous across the Fermi surface. Finally, it is difficult to generate adiabatic trajectories for a liquid metal. The absence of the gap in the densities of electronic states favours the energy transfer from the ionic to the electronic subsystem. Rather than looking here for a definite answer to these difficult and unsolved problems we will introduce some additional approximations that will be justified a posteriori by final results.

L-Si is a suitable model system to be treated by CP. Because of its high melting temperature ($\sim 1700^\circ\text{K}$) [19], measurements on l-Si have been somewhat difficult. In this situation calculation may be of some predictive value. L-Si being a non-simple liquid it has a highly anomalous both pair correlation function $g(r)$ and the static structure factor $S(k)$. On melting the diamond structure contracts by ~ 10 percent [20], the coordination number increases from $N' = 4$ to an unusual value $N' \sim 6.4$ [21, 22], giving rise to a partial collapse of the tetrahedral network. This poses also the question regarding the type of bonding in l-Si. On melting l-Si undergoes a semiconductor-metal transition. These features are consequences of an extremely delicate nature of the Si potential. Not surprisingly, any empirical additive pair potential fails. Empirical potentials including three-body correlations may be successful [23] but they can never describe all the Si phases.

We have performed a constant volume calculation employing eqs. (9) [24]. The only modification was that a Nose' thermostat [25] was applied to the ionic subsystem, i.e. we carried out a constant temperature calculation in a canonical ensemble. A periodically repeated cubic cell with $a = 19.816$ a.u. containing 64 atoms was used. This corresponds to the equilibrium density of l-Si [20]. The average temperature was kept at $T = 1800^\circ\text{K}$, slightly above the melting temperature. The same first-principle non-local norm-conserving pseudopotential as in Sect. III was used [14]. The forces were calculated in the LDA precision [15]. A plane wave representation of the wave functions was used with an energy cutoff of $12 R_y$ in the dual-space formalism [17]. The only point chosen in the BZ sampling was (after a careful testing) the $\mathbf{k} = (0, 0, 0)$ point corresponding to an infinite system limit. The occupation numbers of single-particle orbitals were kept fixed. The fictitious electronic mass μ was set to 300 a.u. In discretizing

eqs. (9) a tiny time step $\Delta t = 7$ a.u. ($\sim 1.7 \times 10^{-16}$ s) was used. The 'mass' of the thermostat was set to $Q = 250000$ a.u. The role played here by the Nose' thermostat is rather unusual — it constantly supplies energy to the ionic subsystem to compensate for the energy that has been transferred to the electronic degrees of freedom. Consequently, to compensate for deviations from the electronic surface, we carry out \sim every optical phonon period a reoptimization of the electronic degrees of freedom. We have been able to follow the system for a total time of ~ 2.0 ps. We stress once more that this calculation is a fully first-principle one where the only experimental input was the density of the liquid.

Here we concentrate mainly on the description of short-range order. The pair correlation function $g(r)$ and the structure factor $S(k)$ are shown in Fig. 2 along with the experimental results [20, 21, 22]. All the difficult features present in the results. Especially, we are able to recover the shoulder on the high- k side of the first peak of $S(k)$ (often attributed to the presence of covalent bonding). The coordination number calculated by integrating $g(r)$ up to the first minimum gives $N' = 6.8$ in very good agreement with the experimental $N' = 6.4$ [21, 22].

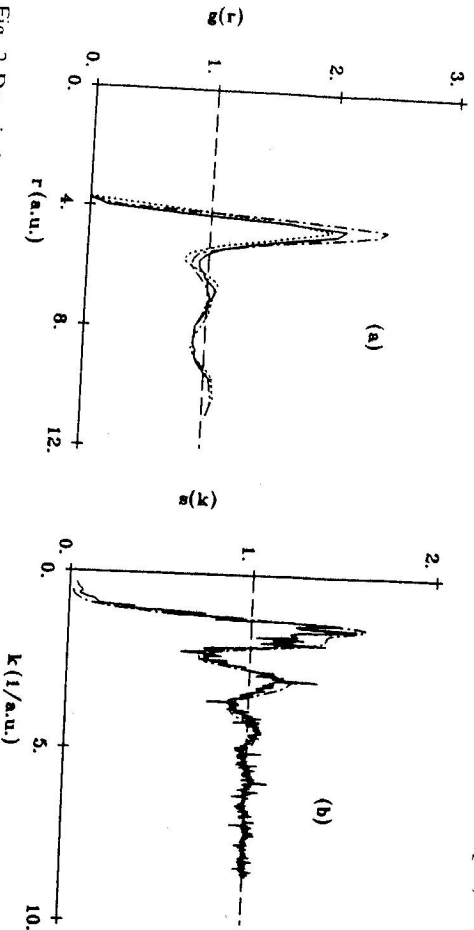


Fig. 2 Description of short-range order in l-Si: a): the pair correlation function; b): the static structure factor. Full line—our calculation, dashed-dotted line—X-ray diffraction experiment [20, 21], dotted line—neutron scattering experiment [22].

This degree of agreement was possible because of the pleasant possibility offered by CP to improve systematically (within DFT in LDA approximation) on interatomic potentials by increasing the cutoffs imposed on the wavefunctions. Thus the precision can be tuned to meet specific requirements. We can also analyse properties not accessible in experiment. The analysis of

the bondangle distribution indicates that l-Si is locally close to a simple hexagonal structure. The analysis of the bonding properties confirms the presence of a strong covalent bonding (l-Si is a 'covalent metal'). According to Phillips [26] the covalent bond can be represented by the Bond Charge (BC) model. In BC the covalent bond is schematized by a point charge midway between neighbouring atoms. The strength of BC is related to the dielectric constant of the material. This feature is depicted by a snapshot of the electronic density in l-Si in Fig. 3 where the presence of BC can be recognized. For comparison the plot of the electronic charge density in the crystalline diamond is also shown in the same Fig. The main difference is that in l-Si the charge is leaking out of the BC and fills up the spaces that are empty in the crystal. More detailed studies of bonding, densities of states, dynamical and transport properties are under way.

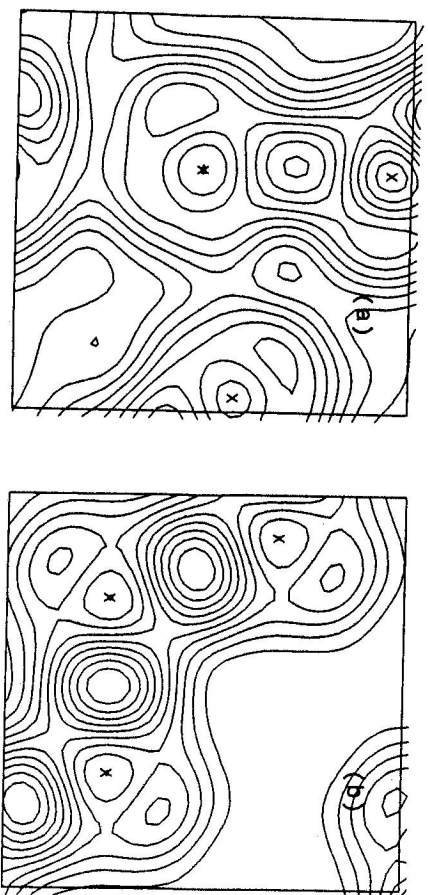


Fig. 3 a): The snapshot of the electronic charge density in l-Si projected on a plane going through three atoms; b): The electronic charge density in the (110) direction in crystalline Si. Crosses indicate the ionic positions.

V. CONCLUSIONS

We started from posing the problem of an efficient calculation of many-body forces within DFT in LDA approximation. We find the CP to be significantly more convenient than the other approaches.

By analysing the MD equations for the one-particle orbitals we arrive at a very effective approach to the standard electronic structure problem. We adapted the well-known CG method to the constrained problem of band-structure. The resulting method is very effective and the efficiency compares very well with other methods, such as DI. The method can be applied to large-scale electronic structure calculations.

As an application of the 'ab-initio' MD we present our results on I-Si. This is probably the first successful application of CP to a metallic system, since previous results have been relatively disappointing [27]. We have an excellent description of short-range order in I-Si. Moreover, we can study also electronic properties, bonding etc., including some properties difficult or impossible to study experimentally.

Since the methods outlined here enable to study realistic systems at a high accuracy level they will play an important role in the future.

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НОВЫЙ ПОДХОД К ВЫЧИСЛЕНИЮ СИЛЫ И СТАНДАРТНОЙ ЗОННОЙ СТРУКТУРЫ

Предлагается обзор объединенного подхода к теории функционала плотности и молекулярной динамики. На основе уравнений молекулярной динамики заново формулируется стандартная проблема электронной структуры и вводится новый метод, основанный на использовании сопряженного градиента. Наконец, используется объединенный подход при изучении короткодействующего порядка и связей в металллическом жидком силиконе на основе первых принципов.