A joint effort with lasting impact

Jürgen Hafner

The ramifications of the Car–Parrinello method, a 25-year-old unified approach to computing properties of materials from first principles, have reached out well-beyond materials science.

**Unified Approach for Molecular Dynamics and Density Functional Theory**

An article by Jürgen Hafner

The article that in 1985 marked the starting point to a series of exciting advances in quantum-based simulations of materials. The article reported an approach — named after the two coauthors and known as Car–Parrinello Molecular Dynamics (CPMD), or simply the Car–Parrinello method — that combined quantum density functional theory (DFT) for the electrons and classical molecular dynamics (MD) for the nuclei, and extended their scope. Before CPMD was available, MD simulations were forced to rely on empirical force fields describing the interactions between the atoms. The basic idea of CPMD was to compute, from quantum mechanics and ‘on the fly’ within a MD trajectory, the forces acting on the atomic nuclei according to the Hellmann–Feynman theorem. CPMD represented a huge step forward because it enabled the simulation of processes in which interatomic bonds are broken and new bonds are formed, such as in chemical reactions and structural phase transitions.

**Real and fictitious dynamics**

CPMD relies on the Born–Oppenheimer (BO) approximation and DFT. The BO approximation allows nuclear and electronic degrees of freedom to be decoupled, assuming that the electrons in each instantaneous configuration of the nuclei are always in their ground state. DFT recasts the intractable complexity of many-electron interactions into the form of an effective one-electron energy that is a unique functional of the electron density. Minimization of the functional with respect to the electronic wavefunctions leads to the well-known Kohn–Sham (KS) equations, which determine the electronic structure of the system. These equations have to be solved self-consistently. Pre-CPMD, the standard solution approach had been based on matrix diagonalization. This required a computational effort that grew rapidly with the size of the system. Furthermore, the entire procedure had to be repeated for a number of atomic configurations to determine the equilibrium atomic geometry.

Owing to the large computational effort, calculating the structural ground state entirely from first principles was affordable for systems with only a small number of configurational degrees of freedom. The extension of first-principles calculations to simulations of the dynamical evolution of a system seemed out of the question.

Car and Parrinello chose an approach entirely different to those existing at that time. They proposed to treat the determination of the KS ground state of the electrons as a complex optimization problem that can be solved using dynamical simulated annealing — a powerful global optimization scheme. Combined with the Newtonian equations of motion of the nuclei, this strategy generates a set of pseudo-Newtonian equations of motion for the coupled electron–ion system:

$$M_{ij} \ddot{R}_i(t) = F_i = -\nabla_{\psi_i} E$$  \hspace{1cm} (2)

where $\mu$ is a fictitious electron mass determining the response of the wavefunctions $\psi_i$, and $\Lambda_{ij}$ are Lagrange multipliers introduced to satisfy orthonormality constraints of the electronic orbitals; $E$ represents the total energy of the system. Nuclear and electronic equations of motion are coupled through the forces $F_i$ acting on the nuclei with masses $M_i$, calculated according to the Hellman–Feynman theorem as the expectation value of the gradient of the KS Hamiltonian ($H_{KS}$):

$$F_i = -\nabla_{\psi_i} E = -\langle \nabla_{\psi_i} H_{KS} \rangle$$  \hspace{1cm} (3)

Although the dynamics of the ions has real physical meaning, that of the electronic degrees of freedom does not; their dynamical evolution is merely a tool for the dynamical simulated annealing approach to find the electronic ground state. When dynamic equilibrium is reached, $\dot{\psi}_i = 0$, and equation (1) is identical, within a unitary transformation, to the KS equations. In this case equations (1) and (2) describe a real physical system, and the forces $F_i$ acting on the nuclei are accurate. To remain close to the ground state it is important that the dynamics of nuclei and electrons are decoupled. Were this not the case, the kinetic energy of the ions would be transferred to the electrons (in accordance to the equipartition theorem), and the system would drift away from the BO energy surface — the potential energy landscape of the adiabatic, decoupled system. As a consequence, the forces calculated according to the Hellmann–Feynman theorem would become inaccurate. In semiconductors and insulators, electrons and ions are effectively decoupled, because electronic excitations require a minimal energy fixed by the width of the energy gap. But metallic systems tend to drift away from this adiabatic ground state and hence their theoretical treatment needs special techniques.

As well as the introduction of the coupled dynamics of electrons and ions (equations (1) and (2)), Car and Parrinello made key suggestions to improve the efficiency of the electronic-structure calculations. They showed that if the KS
The Hamiltonian is decomposed into kinetic ($T$) and potential energy ($V$) terms, $H_{\text{KS}} = T + V$, then $V$ is diagonal in real space and $T$ is diagonal in wavenumber space. Hence, if the operations $V\cdot\psi$ and $T\cdot\psi$, are performed in real and wavenumber space, respectively, the computational effort needed to integrate the electronic equation of motion (equation (1)) is dominated by the fast Fourier transformation between real and wavenumber space. This implies a computational cost that scales as $O(N\text{Min}(M))$, where $N$ is the number of occupied orbitals, and $M$ the number of basis functions ($M \gg N$), in contrast to the $O(M^3)$ scaling of a standard matrix diagonalization.

**Subsequent developments**

The idea that the ground state could be determined by simultaneous optimization of the electronic and nuclear degrees of freedom was not entirely new. Such formalism had already been proposed by Bendt and Zunger, who also developed elaborate corrections to the Hellmann–Feynman forces to compensate for the use of incomplete basis sets and slightly inaccurate, non-self-consistent charge densities. However, although these authors doubted that the electronic ground state could be calculated with sufficient accuracy to derive accurate Hellmann–Feynman forces, Car and Parrinello demonstrated that this could be done, and proposed a practical solution instead of a formal one. Also, the dynamical simulated annealing strategy was not to be the last word; on the contrary, it introduced a new way of thinking about electronic structure calculations that proved to be very inspiring. Teter, Payne and Allan proposed a conjugate-gradient minimization of the total energy for a band-by-band optimization of the electronic orbitals, while Stich et al. proposed a similar procedure for updating all orbitals simultaneously. A few years later, Kresse and co-workers, building on techniques proposed by Pulay for molecular systems, showed that a very efficient approach could be based on a band-by-band minimization of the norm of the residual vector to each eigenstate (this essentially describes the difference between the present approximation to the eigenstate and the exact solutions), combined with an optimized scheme for mixing charge densities and potentials. Slightly ironically, this meant a return to matrix diagonalization. But now the direct diagonalization of a huge Hamiltonian matrix is replaced by an optimized iterative approach to the determination of the occupied eigenstates only. Additionally, the efficiency of the improved methods for the calculation of the electronic structure allows the geometric structure to relax to the ground state after each movement of the nuclei, and to perform molecular dynamics on the BO energy surface for metals as well as for insulators.

The practicability and efficiency of CPMD was first demonstrated by Car and Parrinello in their original article for a system of eight silicon atoms described by a local pseudopotential—a very effective potential that describes the interaction between the valence electrons and the ions, and guarantees that the valence orbitals be orthogonal to the electronic orbitals in the ionic core. With the development of real-space projector techniques, non-local pseudopotentials can be used without loss of efficiency, and with the projector-augmented wave technique (PAW), all-electron calculations for all elements in the periodic table became feasible. Improved DFT functionals, which depend not only on the local density, but systematically incorporate a dependence of the effective one-electron potential on non-local interactions, have also been developed. The implementation of the improved functionals in efficient codes permits the calculation of total energies with better accuracy. Also importantly, parallelization of the computer codes for these methods has made possible their application to increasingly larger system sizes and longer simulation times.

**Ab initio packages**

Nowadays a number of codes for performing first-principles MD simulations are available. Among many, the most noteworthy examples are: the Quantum Espresso program developed by Baroni et al.; the ABINIT code by Gonze and collaborators; the CPMD consortium package developed by Hutter and co-workers on the basis of the original CPMD code; the VASP package by Kresse and colleagues; and the CASTEP package of Payne and co-workers. As well as performing electronic structure calculations and geometry optimizations for large systems (calculations for several-thousand atoms are now possible on medium-size clusters), and MD simulations in various ensembles, these codes include many other functionalities. For instance, the calculation of the linear response to ionic displacements and applied electric fields permits the calculation of phonon dispersion relations, vibrational spectra, and of strain dielectric and piezoelectric tensors. In addition, time-dependent DFT has been implemented within linear-response theory, allowing the calculation of optical excitations. Furthermore, the energies and forces calculated by these programs can also be used in external routines, for instance to determine unknown crystal structures using genetic algorithms and to calculate free-energy differences using thermodynamic integration and constrained MD. Other uses of these programs include searching for transition states in chemical reactions and structural phase transitions using metadynamics or Monte-Carlo-based transition path sampling methods (Fig. 1).

The long-standing goal of computational materials design seems to be close to realization, as demonstrated, for example, by the development of new catalysts free of precious metals for the selective hydrogenation of acetylene, of superelastic and superplastic alloys, and by the selection of the optimal zeolite structure for the disproportionation of xylenes, all guided by ab initio DFT calculations. First-principles calculations inspired by CPMD have had a profound impact not only in materials science, but also in other areas such as the geosciences and biology. In geophysics, for example, the predictions through genetic algorithms of the structure of the high-pressure post-perovskite phase of MgSiO$_3$ (ref. 23; Fig. 2), found at the lower boundary of the Earth’s mantle, explained the origin of the anomalous seismic properties of this layer. An experimental determination of the structure is impossible because such high pressures could never be realized in a laboratory. In biochemistry, ab initio investigations...
of solvent and protein effects on the protonation of the retinal chromophore in the photoreceptor rhodopsin14 (Fig. 3) helped researchers to understand how the receptor reaches the activated state, a process of crucial importance for the visual process in the eyes of vertebrates. A more detailed, fascinating look at the spreading process in the eyes of vertebrates. A more detailed, fascinating look at the visual process in the human eye?

**Present limitations**

Notwithstanding the enormous advances that CPMD has spurred, limitations inherent to DFT remain, the most challenging being the inability to describe dispersion (van der Waals) forces and excited-state energies (bandgaps), and the failure to account for strong electronic correlations in systems with localized \(d\) or \(f\) electrons. Working up the ‘Jacob’s ladder’ of hierarchical DFT functionals19 proves to be difficult and does not solve all problems (there is no ‘heaven of DFT accuracy’, as the top of the ladder is still an approximation to the unknown, exact DFT functional).

Hybrid functionals mixing DFT and exact exchange predict fundamental energy gaps of semiconductors and insulators in very good agreement with experiment20. The good agreement achieved means that the so-called bandgap problem — standard DFT predictions of energy gaps are always too narrow — which has hampered DFT calculations for such a long time, is now solved, opening the way to a predictive ‘computational bandgap engineering’ for semiconductors and solar-cell materials, for example. Very recently, it has been demonstrated that a treatment of dynamical electronic correlations within the so-called random phase approximation provides excellent results for lattice constants, heats of formation and adsorption energies of metallic, semiconducting and insulating systems.30 The theory seamlessly includes van der Waals bonding and should be applicable to systems with up to at least one-hundred atoms. Although there is room for improving the efficiency of the calculations, this is still far from the size of systems that can be handled using standard DFT calculations. Despite the fact that the CPMD method and its successors have provided a great boost to the scaling of the computational effort with the size of the system, the necessity to orthogonalize the electronic orbitals for very large systems will ultimately set a limit to the system size accessible to first-principles calculations. Nevertheless, there have been attempts to cope with this shortcoming. They include embedding strategies (an active core is treated \(ab\) \textit{initio} and embedded in an environment treated at a lower level of theory) and the so-called linear scaling methods that exploit the short-range nature of the KS density matrix31.

**Looking back**

First-principles simulations of materials have undergone dramatic changes since the publication of the CPMD approach 25 years ago. The work by Car and Parrinello not only laid out many new ideas, but also provided a refreshing look to an old problem, inspiring new ways of thinking. Perhaps key to the work that led to CPMD was the synergetic combination of the authors’ expertise in electronic structure calculations and statistical mechanics. In all likelihood their combined background inspired them to consider the calculation of the electronic structure as an optimization problem as suggested by the variational principle of DFT, and guided their search for an efficient solution. Soon after the publication of their article, many different algorithms for the electronic structure problem were proposed and implemented. Superficially, this sometimes led to a return to old techniques, but even when matrix diagonalization and mixing strategies were re-adopted, they had an entirely different aspect: iterative diagonalization and preconditioning led to an algorithm that was orders of magnitude more efficient than the straightforward diagonalization of the past. Assisted by the rapid increase in computational power, and by the development of improved density functionals and efficient post-DFT approaches, static and dynamic first-principles calculations are now firmly established as an essential research tool in a wide range of scientific areas. Who would have thought in 1985, that \(ab\) \textit{initio} DFT calculations would at sometime help to develop new catalysts and photovoltaic materials, solve long-standing problems in the geosciences, and provide deeper insights into the chemical reactions underlying the visual process in the human eye?

Jürgen Hafner is in the Fakultät für Physik and Center for Computational Materials Science, Universität Wien, Sensengasse 8/12, A-1090 Wien, Austria. e-mail: juergen.hafner@univie.ac.at

**References**

11. www.pwscf.org
12. www.abinit.org
13. www.cpmd.org
15. www.caster.org