Nuclear motion is classical

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The notion from ab-initio molecular dynamics simulations that nuclear motion is best described by classical Newton dynamics instead of the time-dependent Schrödinger equation is substantiated. In principle a single experiment should bring clarity. Caution is however necessary, as temperature dependent effects must be eliminated when trying to determine the existence of a zero-point energy.

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Recently [1], we argued that nuclear motion is best described classically instead of using the time-dependent Schrödinger equation. A victory for Car and Parrinello who chose to develop a code which treats the electronic cloud quantum mechanically (using the density functional theory (DFT) approximation) and the motion of the nuclei classically [2]. Car-Parrinello molecular dynamics (CPMD) calculations and, more general, ab-initio molecular dynamics (AIMD) calculations (not necessarily using DFT) were always considered to be an approximation to a proper quantum mechanical treatment of the nuclei which would use the time-dependent Schrödinger equation. To get things sorted: within AIMD there are different ways to describe the propagation of the electrons, in particular, CPMD and BOMD (Born-Oppenheimer MD). For the present consideration this difference is irrelevant. We are focusing in this paper on the motion of the nuclei, not touching the motion of the electrons any. Also it should be mentioned that the whole consideration ignores relativity; for the nuclei relativity can be used just as well, the numerical difference is negligible since the nuclei move slowly, approximately with the speed of sound, far from the speed of light. The term ‘classical’ is used as difference to quantum mechanics, not to relativity.

Why take the simulation of chemical reactions so important in this context? Because the results of such simulations were perfectly unpredictable. Schrödinger developed his equation for the hydrogen atom with one electron only. Pauli added spin and the Pauli principle to describe systems with more than one electron and this all a century ago when it was impossible to check anything numerically with computers. A century later one is used to interpreting orbitals and their imagined motion during a reaction. A lot is guessing with chemical intuition. Our movies frequently confirm this chemical intuition, sometimes no. Sometimes we learn that a multi-step mechanism is a trivial explanation for a difficult to understand reaction pattern.

Nevertheless, that we succeeded to describe a finite number of experiments might be accident and is only a moderately strong argument. But there must be lots of evidence, right? There are molecular vibrations and the spectra are well known. Classical motion means there is no zero-point energy. The well-known $\frac{1}{2}h\nu$ would be missing, independent if one looks at a quadratic potential, or a Morse potential, or if one computes the potential explicitly. Should one not see from the spectra that a quantum mechanical description is clearly superior?

Actually, by fourier transform of CPMD trajectories, it is possible too, to obtain a quantitatively reasonable description of vibrational spectra [3], a convenient approach which can easily also be applied to large molecular systems. (For more quantitative results one has to use lower electron masses and time steps.) The zero-point energy is not directly seen in the spectra, since, like in experiment, only energy differences are measured.

Have a look at some of our movies of highly reactive systems [4] to get a realistic picture of nuclear motion. Even if our pictures are still learning how to run, one gets a general impression. If someone would describe nuclear motion one day more accurately, optically the 3D motion will more or less look the same as in our movies now, not so much will change. At normal temperatures ($T \ll 10000$ K) molecular vibrations only are seen in the spectra, since, like in experiment, only energy differences are measured.

But is there not an isotope effect in nuclear motion? Let us have a look. When are isotope effects observed? What experiment gives a reliable answer? I recommended [1] to directly measure the reaction enthalpy $\Delta H_f$ for the reactions $3\text{H}_2 + N_2 \rightarrow 2\text{N}_3$ and $3\text{D}_2+N_2 \rightarrow 2\text{N}_3$ using calorimetry. The ammonia for-
pend on the mass and for a given potential, also Newton dynamics with the equation reactions is easily observed. It turns out however that tope effect of deuterisation on the velocity of chemical thermodynamic isotope effect. Indeed, this kinetic iso-
prove the zero-point energy via an isotope effect. They used everywhere — that chemists tried with all means to prove the zero-point energy in nuclear motion. The conviction that objects below a certain size must be treated quantum mechan-
entially may have been strong enough to affect the believe in calorimetry experiments. Now let me argue that it is not the size alone which determines the differential equation to be used for the description of a certain object. It may have been a consequence of a simplified believe in quantum theory — the Schrödinger equation must be used everywhere — that chemists tried with all means to prove the zero-point energy via an isotope effect. They searched then for a kinetic isotope effect instead of the thermodynamic isotope effect. Indeed, this kinetic iso-

FIG. 1. Example for the classical treatment of the nuclei with CPMD: HCl dissociates if a field with a linearly decreasing frequency is applied (red line). It relaxes again if instead the frequency of the external field is constant (black line). Our usual methodology was applied (CPMD, LSD, BLYP, Troullier-Martins pseudopotentials, see for example [5]).

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ation changes the bond situation strongly from a triple to single bonds which makes the zero-point energy effect relatively high (3 kcal/mol) compared to other reactions. The water formation from the elements is another example where calorimetry could yield a result that is beyond doubt. The values given in data bases [6, 7] are computed under the assumption that there must be a zero-point energy in nuclear motion. The conviction that objects below a certain size must be treated quantum mechan-
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tive quantum field equation.\[2\] the celebrated Klein-Gordon equation which is a rela-
tivistic quantum field equation.
Car-Parrinello equations:

\[
\left[ \mu \frac{\partial^2}{\partial t^2} - \frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + v_{\text{eff}} \right] \psi_i = \sum_j \epsilon_{ij} \psi_j
\]

(1)

Klein-Gordon equation:

\[
\left[ \frac{\hbar^2}{mc^2} \frac{\partial^2}{\partial t^2} - \frac{\hbar^2}{m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + mc^2 \right] \Psi = 0
\]

(2)

The first set of equations is well tested by all the Car-Parrinello molecular dynamics simulation runs. Obtained are the perfectly real orbitals \(\psi_i\) which depict most concrete a chemical structure or reaction. It is easy to interpret the change of these clouds. Some chemical questions are easier to interpret in terms of localized orbitals, but also these localized orbitals extend over an angstrom. Localization of orbitals down to point charges changes the physics, but can help to illustrate phenomena like charge transfer. It is these perfectly deterministically moving clouds which determine a molecular structure or a chemical reaction, every one of them determined by the effective potential \(v_{\text{eff}}\) formed by all other particles in the system. This should remove the quantum mechanical observation problem.

Numerically there is a lot of problems unsolved. From the comparison of the two equations above it is evident that the fictitious electron masses in CPMD are way too high. Hence it will not be easy to directly simulate electronic excitations. That also accounts to attempts with the time-dependent Schrödinger equation while with perturbation theory this equation is successfully used in describing electronic spectra. So, at the moment there a lots of open questions, but we have a very interesting system of equations to investigate.

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