An Electron Force Field for combined molecular and electron dynamics

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Modern force fields achieve a remarkable accuracy and transferability by massive fits of higher-level density functional calculations. However, they miss access to electronic properties, like electron transfer or electronic polarization and excitations.

The electron force field (EFF) [1], inspired in VSEPR theory [2], includes electrons explicitly but using a drastically simplified, semi-classical description of the maximally localized Wannier electron functions. In this scheme, electrons behave as classical particles with an additional degree of freedom for their width *w* (radius) which has an associated mass of $3m_e$ and a kinetic energy proportional to $1/w^2$. Apart from the long-range electrostatic repulsion, the short-range and system-independent interaction between these “electron balls” (e-balls) is repulsive for parallel-spin electrons (due to Pauli repulsion) and attractive for anti-parallel spin electrons (due to correlation effects), and the interaction between valence e-balls and ion-cores is also repulsive and dependent on the atomic species.

The original EFF of Su and Goddard [1] had a very simple parameterization that made it suitable only for niche applications at high temperature. Our objective is to develop a general and accurate EFF for the simultaneous simulation of molecular and electron dynamics. In our first version, we have restricted ourselves to spline-interpolated pair-wise interactions, fitting them to a variety of properties of molecules and solids, including relaxed atomic geometries, centers and widths of maximally-localized Wannier functions, multipole moments, atomization and ionization energies, and vibration frequencies. Our results show reasonable accuracy for all these properties, as exemplified in Figs. 1 and 2.

Interestingly, the *vibration* frequencies of the e-ball degrees of freedom show a good correlation with experimental electronic *excitations* (Fig. 3). This can be understood in the simple case of the hydrogen atom, where the e-ball oscillation of width and position correspond to 1s-2s and 1s-2p transitions, respectively. This suggests that, despite their simple semi-classical description, the e-ball dynamics can capture much of the true electron dynamics.

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References

[1] J. T. Su and W. A. Goddard. Excited electron dynamics modeling of warm dense matter. Phys. Rev. Lett., **99**, 185003, (2007).

[2] Ronald J. Gillespie and Istv´an Hargittai. The VSEPR Model of Molecular Geometry. Allyn and Bacon, Boston, 1991.

Figures

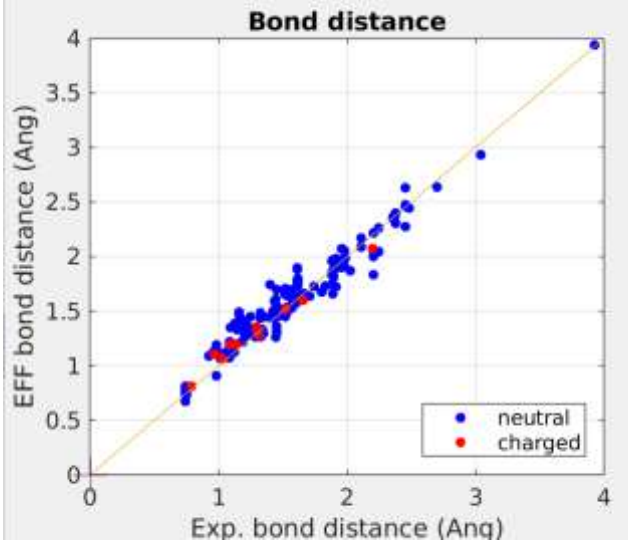

Figure 1. Comparison of experimental and EFF bond lengths of a set of simple molecules and solids.

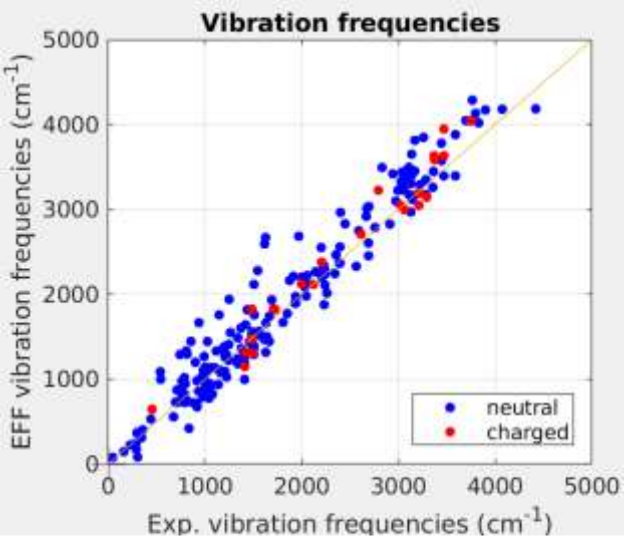

Figure 2. Comparison of experimental and EFF vibration frequencies

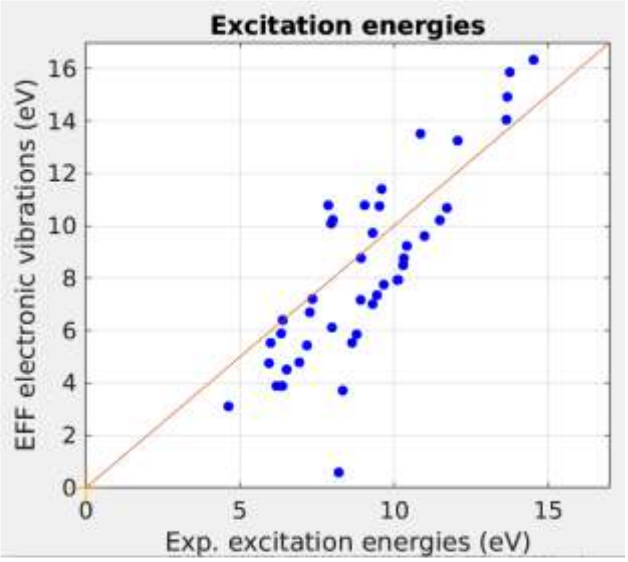

Figure 3. EFF collective electron-ball vibration frequencies of a number of simple molecules compared to experimental electronic excitation energies.