# Su-Goddard Electron Force Field and Car-Parrinello Dynamics

S.B. Trickey[1]

[1] *Quantum Theory Project, Departments of Physics and Chemistry, Univ. of Florida, Gainesville FL 32611-8435*

(Dated: 29 June 2010)

The Su-Goddard [1] effective electon-electron and electron-nucleus potential methodology is recast in the context of approximations to Car-Parrinello dynamics.

PACS numbers:

For molecular dynamics simulation of the thermodynamics of systems of electrons and nuclei, Su and Goddard [1, 2] have introduced what they call an electron force field ("eFF") scheme. The "force field" vocabulary comes most often from bio-molecular simulations with ordinary MD for nuclear motions. Analogous with that work, Su and Goddard introduce an effective potential for both electron-electron interactions and electron-nuclear interactions. The electron-electron part arises from modelling each one-electron state as a single so-called floating spherical gaussian [3]. The gaussian exponent and location then become dynamical variables. In the dynamics, the nuclear coordinates are treated conventionally, while the electron dynamics are handled via gaussian wavepacket dynamics [4].

The Su-Goddard scheme, despite its simplicity, generates a surprisingly good liquid deuterium equation of state, $P$ as a function of $T$ up to 30,000 K. This outcome makes the approach interesting. But I found the presentation somewhat disjoint. After putting it together, it seemed more helpful to formulate the approach as a set of physically motivated approximations to Car-Parrinello dynamics with Kohn-Sham density functional theory [5, 6].

To set notation, for $N_n$ nuclei and $N_e$ electrons, the total system Hamiltonian is

$$\hat{H} = H_n(\mathbb{R},\mathbb{P}) + \hat{H}_{eN}(\mathbf{r}_1,\ldots\mathbf{r}_{N_e};\mathbb{R}) \tag{1}$$

The subscript "eN" indicates electrons in the field of the classical nuclei with coordinates $\mathbb{R}$. The B-O electronic structure problem is

$$\begin{aligned}&\hat{H}_{eN}(\mathbf{r}_1\ldots\mathbf{r}_{N_e};\mathbb{R})\psi_j(\mathbf{r}_1\ldots\mathbf{r}_{N_e};\mathbb{R})\\ &= \mathcal{E}_j(\mathbb{R})\psi_j(\mathbf{r}_1,\ldots,\mathbf{r}_{N_e};\mathbb{R})\end{aligned} \tag{2}$$

In the electronic ground state, the potential on which the classical nuclei move is (Hartree au)

$$\begin{aligned}V(\mathbb{R}) &= E_{nn}(\mathbb{R}) + \mathcal{E}_0(\mathbb{R})\\ E_{nn} &= \frac{1}{2}\sum_{\alpha\neq\beta}\frac{Z_\alpha Z_\beta}{|\mathbf{R}_\alpha - \mathbf{R}_\beta|}\end{aligned} \tag{3}$$

The classical dynamics of the nuclei

$$M_\alpha\ddot{\mathbf{R}}_\alpha = -\nabla_\alpha V(\mathbb{R}) \tag{4}$$

comes from the Lagrangian

$$\begin{aligned}\mathcal{L}(\mathbb{R},\dot{\mathbb{R}}) &= T(\dot{\mathbb{R}}) - V(\mathbb{R})\\ \frac{d}{dt}\frac{\partial\mathcal{L}}{\partial\dot{\mathbb{R}}} - \frac{\partial\mathcal{L}}{\partial\mathbb{R}} &= 0\end{aligned} \tag{5}$$

We suppose the $\mathcal{E}_0(\mathbb{R})$ to be from a ground-state DFT calculation:

$$\begin{aligned}\mathcal{E}_0(\mathbb{R}) &= E_{HKS}[n](\mathbb{R})\\ \frac{\delta E_{HKS}}{\delta n} &= 0\\ \Rightarrow\ \hat{h}_{KS}\varphi_i &= \varepsilon_i\varphi_i \ \rightarrow \sum_i n_i|\varphi_i(\mathbf{r};\mathbb{R})|^2 = n(\mathbf{r};\mathbb{R})\end{aligned} \tag{6}$$

Proceed as usual by introducing a basis $G_\ell(\mathbf{r};\mathbb{R})$ for expansion of the Kohn-Sham orbitals For convenience, assume an orthonormal basis, whence

$$\varphi_i(\mathbf{r};\mathbb{R}) = \sum_{\ell,\mathbb{R}} a_{i,\ell}(\mathbb{R})G_\ell(\mathbf{r};\mathbb{R}) \tag{7}$$

The notation in eq. (7) is a bit overloaded. On the RHS the sum over nuclear positions is to indicate use of a basis set which has subsets centered on each nuclear site. The nuclear positions on the LHS are an explicit display of the fact that the K-S orbitals depend upon the nuclear configuration. Orthonormality then gives

$$\begin{aligned}\int d\mathbf{r}\varphi_i^*(\mathbf{r};\mathbb{R})\varphi_j(\mathbf{r};\mathbb{R}) &= \delta_{ij} \ \Rightarrow\\ \sum_\ell a_{i,\ell}^*(\mathbb{R})a_{j,\ell}(\mathbb{R}) &= \delta_{ij}\end{aligned} \tag{8}$$

In the basis, the variational minimization is equivalent to

$$\begin{aligned}\frac{\partial E_{HKS}}{\partial a_{j,m}^*} &= 0 \ \Rightarrow\\ \det[\mathsf{h} - \varepsilon 1] &= 0\\ h_{\ell,m}(\mathbb{R}) &:= \langle G_\ell(\mathbb{R})|\hat{h}_{KS}(\mathbb{R})|G_m(\mathbb{R})\rangle\end{aligned} \tag{9}$$

The usual solution is by iteration at a given set of nuclear coordinates $\mathbb{R}$:

$$n_{initial} \ \rightarrow\ \hat{h}_{KS} \ \rightarrow \det[\mathsf{h} - \varepsilon 1] \ \rightarrow a_{i,\ell} \ \rightarrow n_{next} \tag{10}$$

cycled until $n_{initial} = n_{next}$. As is well-known, this approach is too slow for routine on-the-fly MD.

Instead, Car and Parrinello conceived the problem differently. For the stipulated basis, the coefficients $a_{i,\ell}$ represent values of a set of quasi-coordinates and each iteration of the cycle in eq. (10) is akin to a time step. The variational condition in the first line of eq. (9) is an energy gradient in the quasi-coordinates $a_{i,\ell}$, and there is a normalization condition on them as well, eq. (8). Thus, if we can assign some kind of "inertia" or resistance to iterative correction to each $a_{i\ell}$ in terms of fictitious masses, then the iterative cycle can be replaced with a Newtonian pseudo-dynamics to optimise the coefficients. Car-Parrinello MD implements this idea via a new *total* Lagrangian

$$\begin{aligned}\mathcal{L}(\mathbb{R},\dot{\mathbb{R}},\mathsf{a}) &= \frac{1}{2}\sum_\alpha M_\alpha \dot{R}_\alpha^2 + \frac{1}{2}\sum_{i,\ell}\mathcal{M}_\ell\left|\frac{da_{i,\ell}}{dt}\right|^2 \\ &\quad -E_{HKS}[\mathsf{a},\mathbb{R}] - E_{nn}(\mathbb{R}) \\ &\quad +\sum_{ij}\lambda_{ij}\left(\sum_{\ell,m}a^*_{i,\ell}a_{j,m}-\delta_{ij}\right) \end{aligned} \quad (11)$$

Application of Lagrange's equations in generalized coordinates to the C-P Lagrangian gives

$$\begin{aligned}\frac{d}{dt}\frac{\partial\mathcal{L}}{\partial\dot{\mathbb{R}}} - \frac{\partial\mathcal{L}}{\partial\mathbb{R}} &= 0 \\ \frac{d}{dt}\frac{\partial\mathcal{L}}{\partial\dot{\mathsf{a}}} - \frac{\partial\mathcal{L}}{\partial\mathsf{a}} &= 0 \end{aligned} \quad (12)$$

which leads to coupled equations

$$\begin{aligned} M_\alpha\ddot{\mathbf{R}}_\alpha &= -\nabla_\alpha V_{BO}(\mathbb{R}) \\ V_{BO} &= E_{HKS}[\mathsf{a},\mathbb{R}] + E_{nn}(\mathbb{R}) \\ &\quad -\sum_{ij}\lambda_{ij}\left(\sum_{\ell,m}a^*_{i,\ell}a_{j,m}-\delta_{ij}\right) \\ \mathcal{M}_\ell\frac{d^2a_{i,\ell}}{dt^2} &= -\frac{\partial E_{HKS}}{\partial a^*_{i,\ell}} - \sum\lambda_{ij}a_{j,\ell} \\ \frac{\partial E_{HKS}}{\partial a^*_{i,\ell}} &= \sum_m n_i a_{i,m}h_{\ell,m} \end{aligned} \quad (13)$$

(Some of the $\mathbb{R}$ dependence is suppressed for clarity of notation.)

To reach the Su-Goddard eFF from the C-P framework requires several distinct steps. First, replace the K-S density by a model density in which each electron has only one basis function, a gaussian normalized to unity, with location $\mathcal{R}_i$ and size (inverse orbital exponent) $s_i$, so that eq. (7) is replaced by

$$\begin{aligned}\varphi_i(\mathbf{r};\mathbb{R}) &= G(\mathbf{r};\mathcal{R}_i;s_i) \\ G(\mathbf{r};\mathcal{R}_i;s_i) &\propto \exp\left[-\left(\frac{1}{s^2}-\frac{2p_s}{s}i\right)(\mathbf{r}-\mathcal{R}_i)^2\right] \\ &\quad \times\exp[i\mathbf{p}\cdot\mathbf{r}] \end{aligned} \quad (14)$$

Here $\mathbf{p} = m_{elec}\,\dot{\mathbf{r}}$, with $m_{elec}$ an effective electronic mass for the dynamics (*not* the physical electronic mass). Eq. (14) is equivalent to Eq. (1.6) in Ref. [2] and the corresponding un-numbered equation on the second page of Ref. [1].

With this expression, one could represent the density and the K-S matrix elements, but the formulation would not meet the orthogonality constraint, Eq. (8). Treating that issue a bit cavalierly for the moment, the corresponding C-P dynamics would look like

$$\begin{aligned} M_\alpha\ddot{\mathbf{R}}_\alpha &= -\nabla_\alpha V_{approxBO}(\mathbb{R}) \\ m_{elec}\frac{d^2s_i}{dt^2} &= -\frac{\partial V_{approxBO}}{\partial s_i} \\ m_{elec}\frac{d^2\mathcal{R}_i}{dt^2} &= -\frac{\partial V_{approxBO}}{\partial \mathcal{R}_i} \\ V_{approxBO} &= E_{HKS}[\mathsf{s},\mathcal{R},\mathbb{R}] + E_{nn}(\mathbb{R}) \\ &\quad -\lambda\left(\int d\mathbf{r}n(\mathbf{r}) - N_e\right) \end{aligned} \quad (15)$$

To connect more clearly with Su and Goddard, we can rewrite these in Hamilton form as

$$\begin{aligned} \dot{\mathbf{P}} &= -\nabla_{\mathbf{R}}V_{approxBO} \\ \dot{\mathbf{p}}_i &= -\nabla_{\mathcal{R}_i}V_{approxBO} \\ \dot{p}_{s_i} &= -\frac{\partial V_{approxBO}}{\partial s_i} \\ \mathbf{P}_\alpha &= M_\alpha\dot{\mathbf{R}}_\alpha \\ \mathbf{p}_i &= m_{elec}\dot{\mathcal{R}}_i \\ p_{s_i} &= m_{elec}\dot{s}_i \\ V_{approxBO} &= E_{HKS}[\mathsf{s},\mathcal{R},\mathbb{R}] + E_{nn}(\mathbb{R}) \\ &\quad -\lambda\left(\int d\mathbf{r}n(\mathbf{r}) - N_e\right) \end{aligned} \quad (16)$$

Apparently the pseudo-dynamics in $s_i$ is problematical [7], though it is a little puzzling as to why in the specific context of Su and Goddard eFF, since it has a Hartree product wave function and then an exchange-energy correction in the force field. In any event, what Su and Goddard do is to follow the Heller-type development, namely to assume that the potential is harmonic, so that the floating gaussians remain gaussian. This leads to the replacement of Eqs. (16) with

$$\begin{aligned} \dot{\mathbf{P}} &= -\nabla_{\mathbf{R}}V_{approxBO} \\ \dot{\mathbf{p}}_i &= -\nabla_{\mathcal{R}_i}V_{approxBO} \\ \dot{p}_{s_i} &= -\frac{\partial V_{approxBO}}{\partial s_i} \\ \mathbf{P}_\alpha &= M_\alpha\dot{\mathbf{R}}_\alpha \\ \mathbf{p}_i &= m_{elec}\dot{\mathcal{R}}_i \\ p_{s_i} &= \frac{3m_{elec}}{4}s_i \\ V_{approxBO} &= E_{HKS}[\mathsf{s},\mathcal{R},\mathbb{R}] + E_{nn}(\mathbb{R}) \\ &\quad -\lambda\left(\int d\mathbf{r}n(\mathbf{r}) - N_e\right) \end{aligned} \quad (17)$$

which is equivalent to Eqs. (1.7) in Ref. [2] (after correction of an obvious missing over-dot on the RHS of each

of the first two equations of the second line) and the corresponding un-numbered equations on the second page of Ref. [1].

The remaining problem is to construct the approximate BO potential. Su and Goddard do this by considering the various energy contributions that arise from the FSGO electron distribution. In my notation (but changing subscripts to "eFF" from "approxBO"), they write

$$V_{eFF} = E_{ke} + E_{nn} + E_{ne} + E_{ee} + E_{Pauli} \tag{18}$$

with

$$\begin{aligned}
E_{ke} &= \frac{1}{2}\sum_i \int d\mathbf{r} |\nabla G(\mathbf{r};\mathcal{R}_i;s_i)|^2 = \frac{3}{2}\sum_i s_i^{-2} \\
E_{nn} &= \sum_{\alpha<\beta} \frac{Z_\alpha Z_\beta}{R_{\alpha\beta}} \\
E_{ne} &= -\sum_{i,\alpha} Z_\alpha \int d\mathbf{r} \frac{|G(\mathbf{r};\mathcal{R}_i;s_i)|^2}{|\mathbf{R}_\alpha - \mathcal{R}_i|} \\
&= -\sum_{i,\alpha} \frac{Z_\alpha}{|\mathbf{R}_\alpha - \mathcal{R}_i|} \mathrm{erf}\left(\frac{\sqrt{2}|\mathbf{R}_\alpha - \mathcal{R}_i|}{s_i}\right) \\
E_{ee} &= \sum_{i<j} \int d\mathbf{r} \frac{|G(\mathbf{r};\mathcal{R}_i;s_i)|^2 |G(\mathbf{r};\mathcal{R}_j;s_j)|^2}{|\mathcal{R}_i - \mathcal{R}_j|} \\
&= \sum_{i<j} \frac{1}{|\mathcal{R}_i - \mathcal{R}_j|} \mathrm{erf}\left(\frac{\sqrt{2}|\mathcal{R}_i - \mathcal{R}_j|}{\sqrt{s_i^2 + s_j^1}}\right) \\
E_{Pauli} &= \sum_{\sigma_i=\sigma_j} E_{ij}^{uu} + \sum_{\sigma_i\neq\sigma_j} E_{ij}^{ud}
\end{aligned} \tag{19}$$

(Obviously this "$E_{Pauli}$" is not the same as the Pauli potential used in the Weizsäcker plus positive correction decomposition of the KS KE [8].) Notice that, rather than anti-symmetrize, they estimate the exchange contribution separately from overlaps of the fsgos, to wit:

$$\begin{aligned}
E_{ij}^{uu} &= \left(\frac{S_{ij}^2}{1-S_{ij}^2} + (1-\rho_{SG})\frac{S_{ij}^2}{1+S_{ij}^2}\right)\Delta T_{ij} \\
E_{ij}^{ud} &= \frac{\rho_{SG} S_{ij}^2}{1+S_{ij}^2}\Delta T_{ij}
\end{aligned} \tag{20}$$

The parameter $\rho_{SG} = -0.2$, while the overlap and anti-symmetrization KE parameters are given by expressions which depend on two scaling numerical parameters, namely

$$\begin{aligned}
S_{ij} &= \left(\frac{2}{\bar{s}_i/\bar{s}_j + \bar{s}_j/\bar{s}_i}\right)^{3/2} \exp[-\bar{\mathcal{R}}_{ij}^2/(\bar{s}_i^2 + \bar{s}_j^2)] \\
\bar{\mathcal{R}}_{ij} &= 1.125\mathcal{R}_{ij} \\
\bar{s}_i &= 0.9 s_i
\end{aligned} \tag{21}$$

and

$$\Delta T_{ij} = \frac{3}{2}\left(\frac{1}{\bar{s}_i^2} + \frac{1}{\bar{s}_j^2}\right) - \frac{2[3(\bar{s}_i^2 + \bar{s}_j^2) - 2\bar{\mathcal{R}}_{ij}^2]}{(\bar{s}_i^2 + \bar{s}_j^2)^2 y} \tag{22}$$

(Some anomalies in Su and Goddard's notation, namely $ij$ on the LHS and 1 and 2 on the RHS, have been cured here.)

With this force field and Eqs. (17), one has the full Su-Goddard scheme.

### Acknowledgments

Work supported in part by the U.S. Dept. of Energy, grant DE-SC0002139.


[1] J.T. Su and W.A. Goddard III, Phys. Rev. Lett. , **99**, 185003 (2007).

[2] J.T. Su, "An Electron Force Field for Simulating Large Scale Excited Electron Dynamics", Ph.D. thesis, Calif. Inst. Techn. 2007.

[3] A.A. Frost, J. Chem. Phys. **47**, 3707 (1967).

[4] E.J. Heller, J. Chem. Phys. **62**, 1544 (1975).

[5] R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985).

[6] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[7] Email, J. Dufty, 28 June 2010.

[8] V.V. Karasiev, R.S. Jones, S.B. Trickey, and F.E. Harris, Phys. Rev. B **80** 245120 (2009).