Supplemental Information for: Non-Adiabatic Study of Dynamic Electronic Effects During Brittle Fracture of Silicon

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THE EFF ENERGY EXPRESSION

eFF overcomes the difficulties of modeling potentially non-adiabatic systems by evaluating the energy of the system as a function of the nuclear coordinates and electron coordinates with a small set of universal electron parameters. This ensures that energy may be partitioned separately into nuclear and electronic degrees of freedom, thus electrons may hop between states without concomitant nuclear motion. We choose to describe nuclei as classical particles and we describe the electrons with a wavefunction of floating spherical Gaussian orbitals similar to the method of Frost [1]. We define our wavefunction as the Hartree product of floating spherical Gaussian orbitals. To do this we include an explicit Pauli energy term which will be described shortly.

$$\Psi \propto \prod_j \exp\left[-\left(\frac{1}{s^2} - \frac{2p_s}{s}\right) (r - \mathbf{x})^2\right] \cdot \exp[i \mathbf{p}_s \cdot \mathbf{x}] \quad (1)$$

With positions $\mathbf{x}$, translational momenta $\mathbf{p}_s$, radial size $s$ and radial momental $p_s$. Rather than use a fully antisymmetrized wavefunction (for which an energy evaluation would require $O(N^4)$ operations), we choose instead a Hartree product wavefunction which will only require $O(N^2)$ operations to compute the energy. Using a Hartree product wavefunction violates the antisymmetry principle for fermions which requires that interchanging any two fermions should cause the sign of the wavefunction to change. In order to satisfy the Pauli principle, we must account for the difference in energy between a full antisymmetrized wavefunction, and a product wavefunction like our Hartree product. To do this we include an explicit Pauli energy term which will be described shortly.

The full potential energy expression is:

$$E = E_{ke} + E_{nuc-nuc} + E_{nuc-elec} + E_{elec-elec} + E_{Pauli} \quad (2)$$

We define the component energies as follows:

$$E_{ke} = \frac{\hbar^2}{m_e} \sum_i \frac{3}{2} \frac{1}{s_i^2} \quad (3)$$

$$E_{nuc-nuc} = -\frac{1}{4\pi e_0} \sum_{i<j} \frac{Z_i Z_j}{R_{ij}} \quad (4)$$

$$E_{nuc-elec} = -\frac{1}{4\pi e_0} \sum_{i,j} \frac{Z_i}{R_{ij}} \text{Erf}\left(\frac{\sqrt{2R_{ij}}}{s_i}\right) \quad (5)$$

$$E_{elec-elec} = \frac{1}{4\pi e_0} \sum_{i<j} \frac{1}{x_{ij}} \text{Erf}\left(\frac{\sqrt{2x_{ij}}}{\sqrt{s_i^2 + s_j^2}}\right) \quad (6)$$

$$E_{Pauli} = \sum_{\sigma_i=\sigma_j} E(\uparrow\uparrow)_{ij} + \sum_{\sigma_i\neq\sigma_j} E(\uparrow\downarrow)_{ij} \quad (7)$$

where (7) comprises the Pauli potential for same spin and opposite spin electrons, respectively. (3) describes the “quantum” electronic kinetic energy, which should not be confused with the classical translational kinetic energy of the electron. The error functions in (5) and (6) arise from the fact that the electron charges are “smeared” over the volume of the Gaussian sphere. Recall that an error function is defined as the integral over a Gaussian and its argument is the upper limit of the integral. This formulation of the Coulomb interactions ensures that the finite sized spherical Gaussians act like point charges at large distances from the other interacting particle. The same spin Pauli energy function is defined as:

$$E(\uparrow\uparrow)_{ij} = \left(\frac{S_i^2}{1 - S_i^2} + (1 - \rho)\frac{S_j^2}{1 + S_j^2}\right) \Delta T_{ij} \quad (8)$$

and the opposite spin Pauli energy is

$$E(\uparrow\downarrow)_{ij} = \left(\frac{(1 - \rho)}{1 + S_{ij}^2}\right) \Delta T_{ij} \quad (9)$$

where $\Delta T$ is the kinetic energy change upon antisymmetrization and $S$ is the overlap of the wavepackets. We can further define these two terms:

$$\Delta T_{ij} = \frac{\hbar^2}{m_e} \left(\frac{1}{s_i^2} + \frac{1}{s_j^2}\right) - \frac{2(3(s_i^2 + s_j^2) - 2x_{ij}^2)}{(s_i^2 + s_j^2)^2} \quad (10)$$

$$S_{ij} = \left(\frac{2}{s_i^2/s_j^2 + s_i^2/s_j^2}\right)^{3/2} \exp(-\frac{x_{ij}^2}{(s_i^2 + s_j^2)}) \quad (11)$$

The last two equations contain the only empirical parameterizations in eFF. We define $\rho = -0.2$, $x_{ij} = x_{ij} \cdot 1.125$
and \( \bar{s}_i = s_i \cdot 0.9 \). These parameters were fit using a small set of hydrocarbons and light metal hydrides. \( \rho \) can be thought of as an orthogonalization parameter while \( \bar{x} \) and \( \bar{s} \) are distance and size scaling parameters, respectively. The Pauli energy functions in (10) and (11) are derived by taking the kinetic energy differences of orthogonalized and non-orthogonalized wavefunctions. The Pauli functions are derived from \( E(\uparrow\uparrow) = E_u - (1 - \rho)E_g \) and \( E(\uparrow\downarrow) = -\rho E_g \). The full derivation of equations (8), (9), (10), and (11) can be found in [2]. eFF uses the difference between Slater and Hartree wavefunctions for the “ungerade” energy expression and the difference between a general valence bond and a Hartree wavefunction to calculate the “gerade” energy expression. The physical interpretation of this effect is more easily understood in terms of orthogonal orbitals. When two same-spin electrons approach one another, their wavefunctions increase in slope to decrease their overlap (they compress in width). This increase in slope increases their gradient and kinetic energy is increased. Wilson and Goddard interpret this change in energy as the Pauli repulsion energy [3]. (7) recovers this energy and ensures that eFF electrons satisfy the Pauli exclusion principle.

The beauty of eFF is in its simplicity. With only three empirical parameters it can reproduce a variety of physical quantities like bond lengths, angles, ionization potentials, and bulk properties. The simple nature of the energy and gradient expressions makes eFF computationally far cheaper than conventional quantum mechanics calculations [2, 4–6].

**THE EFF EQUATIONS OF MOTION AND DYNAMICS**

In 1975 Heller demonstrated wavepacket molecular dynamics (WPMD) as a method for simulating systems in a semi-classical manner [7]. Rather than making a WKB approximation, wherein one assumes that \( \hbar \) is very small [8, 9], he approximated that the wavepacket exists in a local harmonic potential. By substituting a wavefunction of the type in (1) into the time-dependent Schrödinger equation with a harmonic potential, Heller derived the Hamilton equations of motion:

\[
\mathbf{p}_x = m \dot{x} \quad \dot{\mathbf{p}}_x = -\nabla V \tag{12}
\]

These equations are consistent with Ehrenfest’s theorem which states that the average position of a wavepacket follows a classical trajectory. Following the same procedure for the first exponential in (1), and making the assumption that no external potential exists, we can derive the equations of motion for the radial degree of freedom:

\[
p_x = \frac{3}{4} \frac{m_{elec}}{m} \dot{s} \quad \dot{p}_s = -\frac{\partial E}{\partial r} \tag{13}
\]

In eFF, \( m_e \) is defined in three places: (3), (10), and (13). In the former two equations, which correspond to the electron’s potential energy, \( m_e \) is defined as the true electron mass. In the latter equation, it is a user-definable parameter. Changing \( m_e \) in the potential energy terms would affect the sizes and bond lengths of electrons in GS atoms, so it is fixed. Allowing the “dynamical” electron mass in the equations of motion to be adjusted by the user serves a practical purpose: it allows the user to increase the electron’s mass so that it is commensurate with the nuclear masses, and this allows the user to increase the time step of dynamics simulations. It also makes for better coupling in deterministic thermostats. This is not unprecedented; the Landau theory of Fermi liquids uses heavy quasiparticles that obey Fermion statistics and the electron mass is adjustable in semi-classical theories of electron transport in semiconductors. It is prudent to attempt simulations using both the real electron mass, and a larger, user-defined electron mass. The factor of 3/4 in (13) arises directly from the substitution of a Gaussian wave packet into the time dependent Schrodinger equation. These equations are exact for harmonic potentials, and it was shown that they performed well for simple anharmonic potentials like the double well potential [2]. We can use the energies and forces from the electron force field in conjunction with this WPMD scheme as a fully functioning molecular dynamics method.

**RATIONALIZATION OF THE CORE PSEUDOPARTICLE-VALENCE ELECTRON PAULI REPULSION TERM**

Our effective core potential removes ten core electrons and an equal number of protons from silicon each silicon atom and replaces them with a pseudoparticle. The pseudoparticle has a 4+ charge and the mass of a silicon atom. Equation 1 in the manuscript is the general form of the Pauli repulsion between a valence electron and the silicon core pseudoparticle. The purpose of this term is to approximate the Pauli repulsion between the ten core electrons of a silicon atom and any other electron in the simulation.

Consider the eFF wavefunction corresponding to a single silicon atom; it has the form of the wavefunction in equation (1). We can rewrite this as a product of core and valence electrons:

\[
\Psi = \prod \Psi_{\text{core}} \prod \Psi_{\text{valence}} \tag{14}
\]

The electron density corresponding to the core electrons must be removed and replaced with an analytic function describing the Pauli repulsion between the collective core electron density and valence electrons (or other atom’s electrons). The core electron wavefunction is just the
product of each basis function for the core electrons:

$$\Psi_{\text{core}} = \prod_{j}^{N_{\text{core}}} \exp\left[-\frac{(r - x_j)^2}{s_j^2}\right]$$

(15)

From equations (8) and (9) it is evident that the Pauli energy is proportional to $S^2$, the squared overlap between the floating Gaussian functions. Consider the the overlap, $S$, between the core electrons and a single valence electron:

$$S = \int_{-\infty}^{\infty} \Psi_{\text{core}}(r - x) \Psi_{v1}(x) dx = \int_{-\infty}^{\infty} \prod_{j}^{N_{\text{core}}} \exp\left[-\frac{(r - x_j)^2}{s_j^2}\right] \Psi_{v1}(x) dx$$

(16)

This is just the convolution of several Gaussian functions, and the convolution of two or more Gaussian functions is merely another Gaussian function. For this reason we have defined the core-valence Pauli energy term in the following manner:

$$E_{\text{Pauli,Ce}}(r, s) = a \exp\left[-\frac{br^2}{(c^2 + s^2)}\right]$$

(17)

where the function is centered on the core-pseudoparticle and $r$ is the distance between the valence electron and the core pseudoparticle, and $s$ is the radius of the valence electron. The fitting parameters, $a$, $b$, and $c$, serve to approximate the effects of the Pauli interactions between the core electrons and the valence electron, and also to parameterize the Pauli interactions between the core electrons.

**NEW POTENTIAL TERMS**

In addition to the Pauli potential term described here and in the paper, we have introduced new electrostatic potential terms for the interaction of core pseudoparticles, normal nuclei and valence electrons.

$$E_{C,N} = \frac{1}{4\pi\epsilon_0} \sum_{i,j} Z_i Z_j R_{ij} \text{Erf} \left[\frac{\sqrt{2} R_{ij}}{r_{\text{core,j}}^2}\right]$$

(18)

$$E_{C,e} = \frac{1}{4\pi\epsilon_0} \sum_{i,j} Z_i Z_j R_{ij} \text{Erf} \left[\frac{\sqrt{2} R_{ij}}{\sqrt{r_{\text{core,j}}^2 + r_{e,j}^2}}\right]$$

(19)

$$E_{C,C} = \frac{1}{4\pi\epsilon_0} \sum_{i,j} Z_i Z_j R_{ij} \text{Erf} \left[\frac{\sqrt{2} R_{ij}}{\sqrt{r_{\text{core,j}}^2 + r_{\text{core,j}}^2}}\right]$$

(20)

In equations (18) and (19), and (20), $Z$ is the particle charge, $R_{ij}$ is the distance between each particle, and $r$ refers to the particle radius. The subscripts $N$, $C$, and $e$ refer to nuclei, core pseudoparticles, and electrons, respectively.

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in the bulk material from our per atom stress tensor. Using the crack tip position from the previous section and the Young’s modulus, computed from the slope of our stress strain curve, we calculate the strain energy release rate:

\[ G = 1.12^2 \pi P_{xx}^2 a/E^2 \]  

(21)

Where \( P_{xx} \) is the uniaxial stress, \( E \) is the Young’s modulus, and \( a \) is the crack tip position. We set the Griffith critical load, \( G_c = G \) at the onset of fracture. The stress intensity factor can be determined from the same quantities. \( K_{ic} \) is computed similarly:

\[ K_{ic} = \sqrt{G_c E (1 - \nu^2)} \]  

(22)

In this case \( \nu \) is Poisson’s ratio and all other variables have the same meaning.

**ELECTRON DYNAMICS**

**FIG. 2.** The kinetic energy history of select electrons during fracture. In this representative group of electrons ionized electrons are represented in color while non-ionized surface and bulk electrons are in black.

**FIG. 3.** The x-components of a few electrons’ translational velocity. In this representative group of electrons ionized electrons are represented in color while non-ionized surface and bulk electrons are in black. The electrons correspond directly to the plots in the manuscript.

**FIG. 4.** The y-components of a few electrons’ translational velocity. In this representative group of electrons ionized electrons are represented in color while non-ionized surface and bulk electrons are in black. The electrons correspond directly to the plots in the manuscript.

**DYNAMIC ELECTRON YIELD**

In figure 7 we show the number of ionized electrons at each time point in our crack trajectories. Electron are ionized if the sum of their potential and kinetic energy exceeds zero:

\[ E = E_{ke} + 2 \cdot E_{pe} - \frac{3}{2} \cdot \frac{1}{s^2} > 0 \]  

(23)

In eFF each electron’s potential energy is recorded as half the sum of its pairwise interactions with other particles plus its electronic kinetic energy, the second term in the middle expression. To correctly account for the potential energy we must multiply \( E_{pe} \) by two. We subtract the electronic kinetic energy \( 3/2 \cdot 1/s^2 \) because doubling the potential energy doubles the electronic kinetic energy which is implicitly included in each particles potential energy (see [6] for further details on the eFF Hamiltonian).
STRESS NEAR THE CRACK TIP

A significant (orders of magnitude) amplification of stresses near the crack tip is predicted from our eFF silicon fractures, which is consistent with the existence of a mathematical "singularity" as represented in continuum fracture models. Figure 8 shows the distance dependence of the stress tensor component $\sigma_{xx}$ at distances $r$ from the crack tip. The per-atom stresses were summed in cylindrical shells radiating outward from the crack tip and normalized according to the number of particles in each shell. An arbitrary fit of $K_I/\sqrt{2\pi r}$ is provided as reference. Even though the eFF total cell stress is correct, a per particle measurement of stress that included electrons and nuclei would be difficult to validate. The $+/-$ oscillations away from the crack tip, in this single time snapshot, are due to changes in direction of the crack propagation due to the discrete nature of atomic fracture propagation. These would be averaged out over multiple snapshots.

VALIDATION OF THE PSEUDOPOTENTIAL FIT

The computed values for properties included in our training set match well with experimental references. Several geometric parameters for small hydrides were in-
TABLE I. Fit properties (kcal/mol).

<table>
<thead>
<tr>
<th>Property</th>
<th>Experiment</th>
<th>eFF1</th>
<th>eFFcore</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiH&lt;sub&gt;3&lt;/sub&gt;-H [kcal/mol]</td>
<td>91.7</td>
<td>164.5</td>
<td>92.8</td>
</tr>
<tr>
<td>H&lt;sub&gt;3&lt;/sub&gt;Si-SiH&lt;sub&gt;3&lt;/sub&gt; [kcal/mol]</td>
<td>76.7</td>
<td>185.3</td>
<td>74.7</td>
</tr>
<tr>
<td>Si-H [Å]</td>
<td>1.47</td>
<td>1.47</td>
<td>1.48</td>
</tr>
<tr>
<td>Si-Si [Å]</td>
<td>2.32</td>
<td>2.4</td>
<td>2.32</td>
</tr>
<tr>
<td>lattice constant [Å]</td>
<td>5.4</td>
<td>6.2</td>
<td>5.4</td>
</tr>
</tbody>
</table>

TABLE II. Emergent material properties.

<table>
<thead>
<tr>
<th>Method</th>
<th>Experiment</th>
<th>eFF1</th>
<th>eFFcore</th>
</tr>
</thead>
<tbody>
<tr>
<td>ionization potential [eV]</td>
<td>8.2</td>
<td>7.9</td>
<td>8.0</td>
</tr>
<tr>
<td>Si&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt; rotational barrier [kcal/mol]</td>
<td>1.12</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>bulk modulus [GPa]</td>
<td>100</td>
<td>200</td>
<td>201</td>
</tr>
<tr>
<td>yield strength [GPa]</td>
<td>7</td>
<td>-</td>
<td>15</td>
</tr>
</tbody>
</table>

Table III provide several bond dissociation energies for eFF and eFFcore compared to experiment and quantum mechanics. eFFcore vastly improves the computed bond energies for silicon and silicon hydrides.

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