SUPPLEMENTARY DOCUMENT

First-Principles Approach to Finite Element Simulation of Flexible Photovoltaics

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Theory:

From a first-principles perspective, the electronic properties which characterize the transport of charges in a device are modeled by theoretically generating the total charge density (n_i) of the HTL. This can be solved using the density functional theory approach.

The single-particle Kohn–Sham equation is expressed as:

$$\hat{\mathrm{H}}\,\psi_i(r_i) = \epsilon_i(r_i)\psi_i(r_i) \tag{S1}$$

$\hat{\mathrm{H}}$ is the Hamiltonian operator, ψ_i is the Kohn–Sham (KS) orbital, ϵ_i is the (KS) orbital energy, and r_i represents the distance between two electrons.

The Hamiltonian operator is written as:

$$\hat{\mathrm{H}} = T_{KS} + V_{ext} + V_H + V_{XC} \tag{S2}$$

T_{KS} is the kinetic energy of non-interacting particles in the KS orbitals, V_{ext} is an external potential of non-interacting electrons, V_H is the Hartree potential due to

electrostatic interactions, and V_{XC} is the exchange-correlation potential which includes all the remaining unknown terms. The kinetic energy is given explicitly as a function of the orbitals; however, it must be a unique functional of the charge density when the Hohenberg–Kohn arguments are applied. The kinetic energy is expressed as:

$$T_{KS}[n_i] = -\frac{\hbar^2}{2m}\sum_i \int \psi_i^* \nabla^2 \psi_i dr_i, \tag{S3}$$

The expression for the Hartree potential is also obtained as:

$$V_H[n_i] = e\int \frac{n_i}{|r_i - r_i'|} dr_i' \tag{S4}$$

And the ground state energy becomes:

$$\epsilon_i = T_{KS} + \int (V_{ext} + V_H + V_{XC})\ dr_i \tag{S5}$$

We can finally write the Kohn–Sham equation as:

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V_{ext} + V_H + V_{XC}\right)\psi_i(r_i) = \epsilon_i \psi_i(r_i) \tag{S6}$$

A delocalized basis set is used to perform the calculation; hence, a plane wave basis is selected. The self-consistent solution of the wavefunction and its complex conjugates give the electron density of the system.

$$n_i = \sum_i \psi_i^* \psi_i = \sum_i |\psi_i|^2 \tag{S7}$$

According to the Fermi–Dirac statistics, at temperature T, the concentration of electrons n_o at the bottom of the conduction band is given as:

$$n_o = N_c f(E_c) \tag{S8}$$

where N_C is the density of states in the conduction band and $f(E_c)$ is the Fermi–Dirac distribution function which describes the distribution of electrons in the conduction band. For high accuracy, the distribution function can be expressed as:

$$f(E_c) = \frac{1}{\exp\left(\frac{E_c - E_F}{k_B T}\right) + 1} \approx \exp\left(-\frac{E_c - E_F}{k_B T}\right) \tag{S9}$$

Therefore, the electron density in the conduction band is written as:

$$n_o = N_c \exp\left(-\frac{E_c - E_F}{k_B T}\right) \tag{S10}$$

For the valence band, the deficiency of electrons from the saturated situation gives rise to mobile carriers called holes. Similarly, the hole density is given as:

$$p_o = N_v[1 - f(E_v)] \approx N_v \exp\left(-\frac{E_v - E_F}{k_B T}\right) \tag{S11}$$

N_V is the density of states in the valence band, and $f(E_v)$ is the distribution function in the valence band. It is crucial to note that the product, $n_o p_o$, is independent of the Fermi level; therefore, combining (S10) and (S11), we obtain:

$$n_o p_o = N_c N_v \, exp\left(-\frac{E_g}{k_B T}\right) \tag{S12}$$

For a material, even with impurities, the total charge density is:

$$n_i^2 = n_o p_o \tag{S13}$$

The total charge density can be expressed as:

$$n_i = (N_C N_V)^{\frac{1}{2}} \, exp\left(-\frac{E_g}{2k_B T}\right) \tag{S14}$$

E_g is the energy band gap of the semiconductor, and k_B is Boltzmann's constant.

The continuity equation for PV cells which describes the operation of the device is expressed as:

$$\frac{\partial n_i}{\partial t} + \nabla.(n_i v) = G - R \tag{S15}$$

where t is the time, v is the velocity of the charge carriers, G is the generation rate, and R is the recombination rate.

The number of photons absorbed per unit volume, per unit time, $G(x)$, is given by:

$$G(x) = \alpha I_o e^{-\alpha x} \tag{S16}$$

where α is the absorption coefficient of the material, I_o is the incident light intensity, and x is the depth in the material where the absorption occurred. In organic PV, absorbed photons generate excitons, which dissociate into free charge carriers. The efficiency of exciton generation, η_{gen}, and the probability of exciton dissociation, η_{diss}, are important factors. The generation rate of excitons, G_{ex}, can be expressed as:

$$G_{ex}(x) = \eta_{gen}\alpha I_o e^{-\alpha x} \tag{S17}$$

The rate at which excitons dissociate into free charge carriers, G_{free}, can then be written as:

$$G_{free}(x) = \eta_{diss}G_{ex}(x) = \eta_{diss}\eta_{gen}\alpha I_o e^{-\alpha x} \tag{S18}$$

To find the total generation rate of free charge carriers, G, integrate $G_{free}(x)$ over the thickness of the active layer, d:

$$G = \int_0^d G_{free}(x)dx = \eta_{diss}\eta_{gen}\alpha I_o \int_0^d e^{-\alpha x}dx \tag{S19}$$

Evaluating the integral:

$$G = \eta_{diss}\eta_{gen}I_o(1 - e^{-\alpha d}) \tag{S20}$$

The total current density (J_{total}) in the PV device is the sum of the ohmic current density (J_σ) and the local dynamic diffusion current density (J_{diff}).

$$J_{total} = k_B T\left(\mu_e(x) - \mu_p(x)\right)\frac{dn_i(x)}{dx} + qn_i(x)\left(\mu_e(x) + \mu_p(x)\right)E(x) \tag{S21}$$

In an open circuit configuration, the semiconductor has no current flowing across it; therefore, J_{total} is zero. This means that J_{diff} must negate J_{σ}.

$$J_{\sigma} = -J_{diff} \tag{S22}$$

This is written in full as:

$$qn_i(x)\big(\mu_e(x) + \mu_p(x)\big)E(x) = -k_B T\left(\mu_e(x) - \mu_p(x)\right)\frac{dn_i(x)}{dx} \tag{S23}$$

Now, we can have an expression for the electric field as:

$$E(x) = \frac{-k_B T}{q}\left(\frac{\mu_e(x) - \mu_p(x)}{\mu_e(x) + \mu_p(x)}\right)\frac{1}{n_i(x)}\frac{dn_i(x)}{dx} \tag{S24}$$

The electric field creates a potential difference between any two points in the semiconductor. Assuming positions x_1 and x_2, the potential difference (V) between them will be:

$$V = -\int_{x_1}^{x_2} E(x)dx, \tag{S25}$$

further expressed as:

$$V_{OC} = \int_{x_1}^{x_2} \frac{k_B T}{q}\left(\frac{\mu_e(x) - \mu_p(x)}{\mu_e(x) + \mu_p(x)}\right)\frac{1}{n_i(x)}\frac{dn_i(x)}{dx}dx \tag{S26}$$

Equation (S26) gives the general form for the open-circuit voltage between two points by a carrier density gradient.

Finally, the Shockley equation is used to obtain the I–V characteristics of the PV device.

$$J = J_0\left[exp\left(\frac{eV}{nk_B T}\right) - 1\right] \tag{S27}$$

where J is the current density, J_0 is the reverse saturation current, e is the elementary charge, V is the voltage, and n is the ideality factor.