Jumping Kinetic Monte Carlo: Fast and Accurate Simulations of Partially Delocalized Charge Transport in Organic Semiconductors

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ABSTRACT: Developing devices using disordered organic semiconductors requires accurate and practical models of charge transport. In these materials, charge transport occurs through partially delocalized states in an intermediate regime between localized hopping and delocalized band conduction. Partial delocalization can increase mobilities by orders of magnitude compared to those with conventional hopping, making it important for the design of materials and devices. Although delocalization, disorder, and polaron formation can be described using delocalized kinetic Monte Carlo (dKMC), it is a computationally expensive method. Here, we develop jumping kinetic Monte Carlo (jKMC), a model that approaches the accuracy of dKMC for modest amounts of delocalization (such as those found in disordered organic semiconductors), with a computational cost comparable to that of conventional hopping. jKMC achieves its computational performance by modeling conduction using identical spherical polarons, yielding a simple delocalization correction to the Marcus hopping rate that allows polarons to jump over their nearest neighbors. jKMC can be used in regimes of partial delocalization inaccessible to dKMC to show that modest delocalization can increase mobilities by as much as 2 orders of magnitude.

Charge transport is easily modeled in perfectly ordered materials, where charges travel in delocalized bands, and in perfectly disordered ones, where localized charges hop from one site to another. However, many promising materials, such as organic semiconductors, lie in the intermediate transport regime, where charge transport occurs by hops between partially delocalized states. In these materials, both static disorder and polaron formation localize charges, and partially delocalized states arise when this localization is insufficient to reduce the state to one molecule. Understanding intermediate-regime transport is especially important in organic semiconductors, where it underpins the most conductive disordered materials and devices.

State-of-the-art models of partially delocalized charge transport use quantum-mechanical treatments, which can make them computationally expensive. The most detailed models are atomistic simulations such as fragment orbital-based surface hopping and coupled electron–ion dynamics. Coarse-graining to reduce computational cost gives effective-Hamiltonian models such as transient localization, an adaptive hierarchy of pure states equations, density matrix renormalization group approaches, network approaches, modified Redfield approaches and polaron-transformed Redfield approaches. Nevertheless, the computational cost of these models limits them to small systems (usually in one or two dimensions) or short time scales. Recently, we developed delocalized kinetic Monte Carlo (dKMC), a quantum-mechanical model that can describe charge transport in disordered materials on mesoscopic scales and in three dimensions while including the three essential ingredients: disorder, partial delocalization, and polaron formation. dKMC demonstrates the importance of delocalization in disordered charge transport, explaining order-of-magnitude increases in mobility over that of conventional hopping. However, despite the large computational savings of dKMC compared to other quantum-mechanical treatments, it remains expensive, making it impractical for simulations of highly delocalized states in three dimensions or on device scales, where the cost scales exponentially with the number of particles.

Here, we develop jumping kinetic Monte Carlo (jKMC), a practical model of intermediate-regime charge transport of modestly delocalized carriers, whose speed is comparable to that of hopping models and whose accuracy is comparable to that of dKMC. We do so by treating the partially delocalized states as a lattice of identical, spherical polarons (Figure 1), allowing us to avoid the most computationally expensive aspects of dKMC. The result of jKMC is a simple
Figure 1. jKMC model of partially delocalized charge transport in disordered materials. (a) The starting point of jKMC is a lattice of sites with disordered energies (different colors) and nearest-neighbor couplings \( J \), coupled to the environment (motion lines). (b) Diagonalizing the Hamiltonian yields delocalized polarons with a distribution of shapes and sizes. A suitably chosen neighborhood (dashed line) is used to average the polaron sizes into a uniform size for jKMC. (c) jKMC uses the neighborhood-averaged polaron size to represent partially delocalized transport as hopping between uniformly sized spherical polarons. This delocalization allows polarons to jump over their nearest neighbors.

delocalization correction to the Marcus hopping rate that can be included in any transport model. Applied to charged transport, it reveals even greater mobility enhancements for states that are too delocalized to be modeled in dKMC.

Conventional models of charge transport in disordered materials commonly use kinetic Monte Carlo (KMC) simulations to model hopping between an array of sites, usually a lattice. Disorder is commonly introduced by assigning to each site an independent random energy from a Gaussian density of states (DOS) of width \( \sigma \). The probability of each hop and the time taken are determined by the hopping rates, usually expressed using nearest-neighbor Marcus or Miller–Abrahams rates

\[
\begin{align*}
\kappa_{ij}^{\text{Marcus}} &= \frac{2\pi T^2}{\sqrt{4\pi k_B T}} \exp \left\{ -\frac{(E_i - E_j + \lambda)^2}{4k_B T} \right\} \\
\kappa_{ij}^{\text{MA}} &= \begin{cases} 
\nu_0 e^{-\frac{(E_j - E_i)}{k_B T}} & \text{if } E_j > E_i \\
\nu_0 & \text{otherwise}
\end{cases}
\end{align*}
\]

where \( J \) is the electronic coupling between neighboring sites, \( \lambda \) is the reorganization energy, \( \nu_0 \) is the hopping attempt frequency, \( T \) is the temperature, \( E_i \) and \( E_j \) are the energies of the initial and final sites, respectively, and we have set \( \hbar = 1 \). These rates are widely used due to their simplicity, low computational cost, and ability to explain, for example, the electric-field and temperature dependence of mobilities in certain disordered materials.

The nearest-neighbor rates presented above are often modified to model partially delocalized charge transport by using them to simulate non-nearest-neighbor hopping. To do so, \( \kappa_{ij}^{\text{Marcus}} \) and \( \kappa_{ij}^{\text{MA}} \) are usually multiplied by a phenomenological tunnelling factor, \( e^{-d_y} \), where \( d_y \) is a fitting parameter called the inverse localization radius and \( d_y \) is the hopping distance. The tunnelling factor was originally developed for impurity conduction in crystalline materials, where it correctly captures the overlap of exponentially decaying tails of distant impurity sites. However, this justification is not valid for densely packed organic semiconductors, where there are many sites in the proximity of each other. However, we will see that jKMC results in an expression similar to the tunnelling factor for realistic amounts of delocalization in organic semiconductors.

Instead of a phenomenological factor, dKMC models the fundamental processes giving rise to partially delocalized transport. dKMC uses the secular polaron-transformed Redfield equation (sPTRE) to model transport between delocalized polarons. It assumes an effective, tight-binding Hamiltonian for a lattice of sites, where each site is linearly coupled to an identical, independent bath of harmonic oscillators. The polaron transformation is applied to this Hamiltonian, reducing the system–bath coupling and allowing it to be treated by second-order perturbative Redfield theory. Applying this treatment to a system with normally distributed energies and nearest-neighbor electronic couplings \( J \) yields the rate of hopping from polaron \( \nu \) to polaron \( \nu' \)

\[
R_{\nu\nu'} = \sum_{\langle i,j \rangle, \langle i',j' \rangle} 2|J|^2 \text{Re} \langle \langle i| \hat{V}|j' \rangle \langle i'| | \hat{V} |j \rangle \rangle K_{\Delta_{\nu\nu'}}(\omega_{ij})
\]

where \( \nu \) and \( \nu' \) are eigenstates of the polaron-transformed Hamiltonian, \( \langle i, j \rangle \) and \( \langle i', j' \rangle \) are nearest-neighbor pairs of sites, \( \omega_{ij} = E_i - E_j \) is the energy difference between the polarons, and \( K_{\Delta_{\nu\nu'}}(\omega) \) describes the residual system–bath coupling in the polaron frame, as described in section S1 of the Supporting Information. In calculating \( K_{\Delta_{\nu\nu'}}(\omega) \), we assume a super-ohmic spectral density \( J(\omega) = \frac{\lambda}{\omega + \omega_s} e^{-\omega/\omega_s} \), where \( \lambda \) is the reorganization energy and the cutoff frequency \( \omega_s \) is set to 62 meV. This spectral density is commonly assumed for disordered organic semiconductors however, any spectral density can be employed.

Calculating the hopping rate \( R_{\nu\nu'} \) in dKMC requires diagonalizing disordered Hamiltonians to calculate the delocalized polaron states \( |\nu\rangle \), which have irregular shapes and off-lattice positions. Diagonalizing these Hamiltonians becomes the computational bottleneck for dKMC in three dimensions, and at large \( J \) values, the states become too large to be contained within a Hamiltonian that can be diagonalized. jKMC avoids the computational bottleneck of dKMC by avoiding the calculation of all of the polaron states. Instead, it assumes that the polaron wave functions are identical and spherically symmetric. We also assume that the polarons are centered on a cubic lattice with spacing \( a \) and have independent and normally distributed energies (with a mean...
of 0 and a standard deviation of $\sigma$) and that their shapes follow the exponential localization seen in the Anderson model.\textsuperscript{4} Specifically, we take

$$\nu = A \sum_i \exp \left( -\frac{d_{\nu}}{r_{\text{deloc}}} \right)$$

(4)

where $d_{\nu}$ is the distance between the center of polaron $\nu$ and site $i$, $r_{\text{deloc}}$ is the delocalization radius that characterizes the size of the wave function, and $A = \left( \sum_i \exp \left( -2d_{\nu}/r_{\text{deloc}} \right) \right)^{-1/2}$ is the normalization.

Parametrizing jKMC requires choosing a value of $r_{\text{deloc}}$. Our objective is to choose the $r_{\text{deloc}}$ that will yield accurate mobilities. In disordered materials, $r_{\text{deloc}}$ should depend on mean energy ($E$) of the polarons because polaron sizes decrease (on average) as they relax to more localized states lower in the disordered DOS. For example, $r_{\text{deloc}}$ should be larger for an ensemble of randomly occupied polaron states (where $\langle E \rangle = 0$ and many large states in the middle of the DOS are occupied) than for an ensemble of polarons that have reached thermal equilibrium (where $\langle E \rangle = -\sigma^2/k_BT$ and the occupied states are mostly the localized traps).\textsuperscript{1}

To choose $r_{\text{deloc}}$ we relate it to a readily calculated measure of delocalization, the inverse participation ratio

$$\text{IPR}_{\nu} = \left( \sum_i |\langle i|\nu \rangle|^4 \right)^{-1}$$

(5)

which roughly equals the number of sites over which polaron $\nu$ is delocalized. A localized wave function has an IPR of 1, while a wave function spread evenly across $N$ sites ($\langle |i\rangle |^2 = N^{-1/2}$) has an IPR of $N$. The spherical polarons of eq 4 have an IPR of

$$\text{IPR}_{\text{jKMC}} = A^{-2} \left( \sum_i \exp \left( -\frac{d_{\nu}}{r_{\text{deloc}}} \right) \right)^{-1}$$

(6)

an equation that allows us to calculate an $r_{\text{deloc}}$ that reproduces a given IPR.

We set $r_{\text{deloc}}$ using eq 6 on the basis of the mean IPR of the polaron states that participate in charge transport at a given $\langle E \rangle$. This IPR is calculated through an approach we call neighborhood averaging. First, we note that the averaging of the polaron IPRs should be thermally weighted because transport is driven by relaxation to thermal equilibrium. A complete thermal average requires that every state be accessible; however, during the initial stages of transport in a disordered material, the polaron is unable to completely explore the DOS. Instead, if a polaron can explore only a local neighborhood of $N$ polaron states until a particular time, we take the thermal averages of polaron states within that neighborhood. Therefore, we define the effective IPR and the effective energy as

$$\text{IPR}_{\text{eff}}(N) = \left( \frac{1}{Z} \sum_{\nu=1}^{N} \text{IPR}_{\nu} \exp \left( -\frac{E_{\nu}}{k_BT} \right) \right)$$

(7)

$$E_{\text{eff}}(N) = \left( \frac{1}{Z} \sum_{\nu=1}^{N} E_{\nu} \exp \left( -\frac{E_{\nu}}{k_BT} \right) \right)$$

(8)

where $\text{IPR}_{\nu}$ and $E_{\nu}$ are the polaron IPRs and energies, respectively, obtained from the diagonalization of the model Hamiltonian,\textsuperscript{3} $Z = \sum_{\nu=1}^{N} \exp \left( -E_{\nu}/k_BT \right)$ is the partition function, and the average (angle brackets) is taken over an ensemble of disordered energetic landscapes (1000 instances in our calculations). Equations 7 and 8 allow us to obtain an $r_{\text{deloc}}$ for any $\langle E \rangle$ in two steps. First, for a given $\langle E \rangle$, we determine the appropriate neighborhood size $N$ using eq 8, and second, we use that same $N$ in eq 7 to determine the $\text{IPR}_{\text{eff}}$ that can be converted into $r_{\text{deloc}}$ using eq 6.

With $r_{\text{deloc}}$ in hand, we can now substitute the spherical-polaron approximation in eq 4 into the delocalized polaron hopping rate (eq 3). To obtain a simple rate expression, we also assume the high-temperature limit ($k_BT \gg \omega_c$), because many organic semiconductors operate close to this limit.\textsuperscript{36–38}

In addition, the high-temperature limit is the regime of validity of ordinary Marcus theory, and using it reveals the relationship between ordinary KMC and jKMC. Using the spherical-polaron and high-temperature approximations, we obtain the jKMC rate between any two polarons (derivation in section S1 of the Supporting Information)

$$k_{\text{jKMC}}^{\nu \nu'} = k_{\text{Marcus}}^{\nu \nu'} \xi_{\text{deloc}}^{\nu \nu'}$$

(9)

where $k_{\text{Marcus}}^{\nu \nu'}$ is the Marcus rate of eq 1 from polaron $\nu$ to $\nu'$ as if they were nearest neighbors and $\xi_{\text{deloc}}^{\nu \nu'}$ is the delocalization correction

$$\xi_{\text{deloc}}^{\nu \nu'} = A^4 \sum_{\langle ij \rangle} \exp \left[ \frac{-2(d_{\nu i} + d_{\nu j})}{r_{\text{deloc}}} \right]$$

(10)

where the sum runs over nearest-neighbor pairs of sites $i$ and $j$. Hence, the effect of delocalization is to make Marcus rates long-range in a way that depends straightforwardly on delocalization radius $r_{\text{deloc}}$.

In the low-delocalization limit, $\xi_{\text{deloc}}^{\nu \nu'}$ can be simplified by taking only the dominant exponential terms in eq 10, which leads to the simplified jKMC rate (derivation in section S2 of the Supporting Information)

$$\xi_{\text{simplified}}^{\nu \nu'} = \frac{d_{\nu j}}{a} \exp \left[ -\frac{2(d_{\nu i} - a)}{r_{\text{deloc}}} \right]$$

(11)

Simplified jKMC is similar to inserting the phenomenological correction $e^{-2d_{\nu i}}$ into the Marcus rate and can be considered as a rigorous justification of this correction in the limit of small delocalization. However, there are two important differences. First, the distance-dependent exponent is offset by the lattice constant, which ensures that the correct Marcus rate is reproduced for nearest neighbors. Second, there is a new pre-exponential factor $d_{\nu i}/a$ that accounts for the number of terms significantly contributing to the sum in eq 10.

The jKMC rates $k_{\text{jKMC}}^{\nu \nu'}$ can now be used to simulate polaron dynamics. Disordered materials show dispersive transport (mobilities decreasing over time as the polarons relax within the DOS),\textsuperscript{31,37,39,40} which affects how mobilities should be calculated. Conventionally, mobilities in dispersive systems have been calculated at a chosen time $t_p$ (Figure 2a); however, this approach can lead to unrealistic comparisons, because it can predict lower mobilities for systems with stronger couplings $J$, where polarons can reach deeper traps in the DOS within the same $t_p$. To avoid this pitfall, we calculate the mobilities of polarons that have relaxed (on average) to a chosen target energy $E_T$ [i.e., for which $\langle E \rangle = E_T$ (see Figure 2b)]. In particular, in jKMC, we choose the value of $r_{\text{deloc}}$ that is consistent with this target $E_T$. 

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The delocalization enhancements of jKMC remain large over a range of $E_{\mu}$ in both two and three dimensions (Figure 4c,d). The chosen range of $E_{\mu}$ corresponds to the several order of magnitude differences in transport time $t_{f}$ (Figure 4c), showing that the delocalization enhancement persists over a broad range of time scales. For the parameters tested, jKMC agrees with dKMC to a factor of $\sim 2$. Overall, jKMC provides excellent accuracy considering the simplicity of the method, typical uncertainties in the input parameters, and the fact that the mobilities span orders of magnitude and are underestimated by KMC by as much as 100 times.

The values of $r_{\text{deloc}}$ used in jKMC (Figure 4g,h) are within the typical range of its analogue $\gamma^{-1}$ sometimes used in Marcus or Miller–Abrahams models. For the parameters used in Figure 4, we predict $r_{\text{deloc}}/\alpha$ within a range of $0.2–0.6$, whereas three dimensions, where it predicts even larger enhancements in mobility.
the values of $\gamma^{-1}/a$ are typically in the range of 0.1–1. In other words, jKMC is a microscopic justification of phenomenological $\gamma^{-1}$ parameters that are often inserted into hopping models to enable them to fit experimental results.

Figure 5a shows that the delocalization correction can increase mobilities by several orders of magnitude over KMC ($r_{\text{deloc}} = 0$). In Figure 5a, $r_{\text{deloc}}$ is varied independently, isolating its role from those of the other material parameters. The IPRs corresponding to $r_{\text{deloc}}$ are shown in Figure 5b, which remain modest for the significant enhancements in mobility.

The results of simplified jKMC are also shown in panels a and b of Figure 4 (and in Figure S3), showing that eq 11 can be an acceptable approximation for typical delocalizations in disordered organic semiconductors. The simplified jKMC rate leads to the same order of magnitude mobilities as dKMC; however, it tends to slightly systematically overestimate jKMC.

Despite its overall accuracy and the ability to predict the correct trends, jKMC has systematic errors in certain regimes. Panels c and d of Figure 4 show jKMC overestimates mobilities on short time scales (shallow $E_\mu$) and underestimates them at long time scales (deep $E_\mu$). These errors are related to the assumption of a uniform polaron size, which neglects the effect of the distribution of polaron sizes on mobility. At short time scales, where the distribution is wide and the effective IPR is large, jKMC overestimates the escape from localized traps. In contrast, on long time scales where the distribution has narrowed and the effective IPR is small, jKMC underestimates the escape from traps into highly delocalized states. The boundary between these regimes depends on coupling $J$, as shown in panels c and d of Figure 4.

jKMC achieves a computational cost between those of KMC and dKMC. While based on dKMC, jKMC avoids dKMC’s computational bottleneck of having to repeatedly diagonalize Hamiltonians during the dynamics. Instead, it requires only an up-front diagonalization to calculate the effective IPR. Furthermore, jKMC can achieve neighborhood averaging by

Figure 4. jKMC reproduces the large delocalization enhancements explained by dKMC, including the 2 order of magnitude enhancements in mobility over KMC in (a) two and (b) three dimensions. jKMC reproduces dKMC mobilities where the latter are known and extends beyond them to high levels of delocalization in three dimensions. The simplified jKMC rate also predicts mobilities on the same order of magnitude as dKMC. Mobilities are calculated at $E_\mu = -2.5\sigma$ with $\sigma = 150$ meV, $J = 200$ meV, and $T = 300$ K. (c and d) jKMC reproduces the delocalization enhancements of dKMC over KMC across a range of $E_\mu$ values to a factor of $\sim 2$. (e and f) Times $t_{\text{E}}$ taken to reach target energy $E_\mu$ show that the range of $E_\mu$ in panels c and d spans the typical time scales of mesoscopic charge transport. (g and h) Delocalization radii that parametrize jKMC.
diagonalizing fewer and smaller lattices than need to be diagonalized in dKMC. Smaller lattices suffice in jKMC because the effective IPR is heavily weighted toward smaller, diagonalized in dKMC. Smaller lattices suffice in jKMC dynamics of any polaron on the lattice, including highly delocalized states that require large lattices to describe. Nevertheless, the up-front diagonalization remains the computational bottleneck of jKMC at high electronic energies. (a) In both two and three dimensions, varying \( r_{\text{deloc}} \) independently of \( J \) increases the mobility by several orders of magnitude. Therefore, adding delocalization correction \( \xi_{\nu\nu} \) can easily reproduce large mobilities where conventional KMC hopping fails. Results are calculated at \( E_g = -2.5 \sigma \) for \( J = 75 \text{ meV}, \sigma = 150 \text{ meV, } \lambda = 200 \text{ meV, and } T = 300 \text{ K} \). (b) The jKMC IPR depends on only \( r_{\text{deloc}} \) and can be varied to probe the effect of delocalization. Modest amounts of delocalization produce order of magnitude enhancements in panel a.

Figure 5. jKMC delocalization correction can produce large increases in mobilities. (a) In both two and three dimensions, varying \( r_{\text{deloc}} \) independently of \( J \) increases the mobility by several orders of magnitude. Therefore, adding delocalization correction \( \xi_{\nu\nu} \) can easily reproduce large mobilities where conventional KMC hopping fails. Results are calculated at \( E_g = -2.5 \sigma \) for \( J = 75 \text{ meV}, \sigma = 150 \text{ meV, } \lambda = 200 \text{ meV, and } T = 300 \text{ K} \). (b) The jKMC IPR depends on only \( r_{\text{deloc}} \) and can be varied to probe the effect of delocalization. Modest amounts of delocalization produce order of magnitude enhancements in panel a.

In conclusion, jKMC is a practical model of partially delocalized transport that approaches the accuracy of fully quantum approaches with the cost of classical hopping. jKMC includes a simple correction to the Marcus hopping rate, based on a method for estimating the delocalization radius. It reproduces the large increases in mobility predicted by dKMC but can also simulate larger electronic couplings and delocalization in three dimensions. These factors make jKMC an attractive model that could easily be included in any KMC simulation of a disordered material, including future device-scale models that take into account partially delocalized charge transport.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcl.3c00388.
jKMC rate derivation (section S1), simplified jKMC rate derivation (section S2), simplified jKMC results (mobility enhancements and simulation times) (section S3), and effective IPR convergence (section S4) (PDF)

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**Notes**

The authors declare no competing financial interest.

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Jumping Kinetic Monte Carlo: Fast and Accurate Simulations of Partially Delocalised Charge Transport in Organic Semiconductors

Supporting Information

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S1. JKMC RATE DERIVATION

The foundation of jumping kinetic Monte Carlo (jKMC) is the secular polaron transformed Redfield equation (sPTRE) [1, 2], which provides the hopping rate from any polaron $\nu$ to polaron $\nu'$ as

$$ R_{\nu\nu'} = \sum_{(i,j), (i',j')} 2J^2 \text{Re} \left[ \langle \nu| i \rangle \langle j| \nu' \rangle \langle \nu'| i' \rangle \langle j'| \nu \rangle K_{\Delta(i,j,i',j')} (\omega_{\nu\nu'}) \right], $$

(S1)

where $\langle i, j \rangle$ and $\langle i', j' \rangle$ are nearest-neighbour pairs of sites, $J$ is the nearest-neighbour electronic coupling, $\omega_{\nu\nu'} = E_{\nu} - E_{\nu'}$ is the energy difference between polarons, and

$$ K_{\Delta(i,j,i',j')} (\omega) = \int_0^\infty d\tau e^{i\omega\tau} \langle \tilde{V}_{ij}(\tau) \tilde{V}_{i'j'}(0) \rangle_B $$

(S2)

is the half-range Fourier transform of the bath correlation function

$$ \langle \tilde{V}_{ij}(\tau) \tilde{V}_{i'j'}(0) \rangle_B = \kappa^2 (e^{-\Delta(i,j,i',j')} \phi(\tau) - 1), $$

(S3)

where $\Delta(i,j,i',j') = \delta_{ii'} - \delta_{jj'} + \delta_{ji'} - \delta_{ji}$,

$$ \kappa = \exp \left( - \int_0^\infty \frac{d\omega}{\pi} \frac{J(\omega)}{\omega^2} \coth \left( \frac{\omega}{2k_B T} \right) \right), $$

(S4)

and

$$ \phi(\tau) = \int_0^\infty \frac{d\omega}{\pi} \frac{J(\omega)}{\omega^2} \left( \cos(\omega \tau) \coth \left( \frac{\omega}{2k_B T} \right) - i \sin(\omega \tau) \right). $$

(S5)

We assume that the polaron wavefunctions are identical, spherically symmetric, and exponentially decaying in the site basis,

$$ |\nu\rangle = A \sum_i \exp \left( - \frac{d_{\nu i}}{r_{\text{deloc}}} \right) |i\rangle, $$

(S6)

where $d_{\nu i}$ is the distance between the centre of the spherical polaron $\nu$ and site $i$, $r_{\text{deloc}}$ is the delocalisation radius that characterises the size of the wavefunction, and the normalisation prefactor is $A = (\sum_i \exp (-2d_{\nu i}/r_{\text{deloc}}))^{-1/2}$. Substituting the spherical-polaron approximation into the sPTRE yields

$$ R_{\nu\nu'} = \sum_{(i,j), (i',j')} 2J^2 A^4 \text{Re} \left[ K_{\Delta(i,j,i',j')} (\omega_{\nu\nu'}) \right] \exp \left( - \frac{d_{\nu i} + d_{\nu' i'} + d_{\nu' i} + d_{\nu i}}{r_{\text{deloc}}} \right). $$

(S7)

To simplify this expression, we assume the high-temperature limit ($k_B T \gg \omega_c$) in eq. (S5), using $\coth(\omega / 2k_B T) \approx 2k_B T / \omega$ to obtain

$$ \phi(\tau) = \int_0^\infty \frac{d\omega}{\pi} \frac{J(\omega)}{\omega^2} \left( \frac{2k_B T}{\omega} \cos(\omega \tau) - i \sin(\omega \tau) \right). $$

(S8)

$\phi(\tau)$ enters the integral in eq. (S2) through an exponential, meaning that the integral will be dominated by contributions where $\phi(\tau)$ achieves the maximum real values. This maximisation occurs when $\cos(\omega \tau) \approx 1$, i.e., when $\omega \tau \ll 1$. Therefore, we take the Taylor expansions of $\cos(\omega \tau)$ and $\sin(\omega \tau)$ in eq. (S8) to yield

$$ \phi(\tau) = 2k_B T x_3 - (k_B T \tau^2 + i\tau)x_1, $$

(S9)
where
\[
x_n = \int_0^\infty \frac{d\omega}{\pi} \frac{J(\omega)}{\omega^n}
\]  
(S10)

Similarly, the high-temperature limit of eq. (S4) is
\[
\kappa^2 = e^{-4k_B T x_3},
\]  
(S11)

which is exponentially small at high \( T \).

Therefore, in the high-temperature limit, the bath correlation function becomes
\[
\langle \hat{V}_{ij}(\tau) \hat{V}_{i'j'}(0) \rangle_B = e^{-4k_B T x_3} \left( e^{-\Delta(i,j,i',j') x_3} - 1 \right),
\]  
(S12)

where the coefficient \( \Delta(i,j,i',j') \) assumes integer values between \(-2\) and \(2\). Of these, the \( \Delta(i,j,i',j') = -2 \) contributions (i.e., \( i = j' \) and \( j = i' \)) dwarf the others, and are the only ones negative and large enough to ensure that the \( \kappa^2 \)

![Graph](image.png)

Figure S1. Comparison of different \( K_{\Delta(i,j,i',j')}(\omega) \), shown as functions of the polaron energy difference \( \omega_{\nu\nu'} \). Results are calculated using the spectral density \( J(\omega) \) given in the main text for \( \lambda = 200 \text{ meV} \) and (a) the parameters in this work \((T = 300 \text{ K}, \omega_c = 62 \text{ meV})\), (b) at higher temperature \((T = 3000 \text{ K})\), and (c) at lower cutoff frequency \((\omega_c = 31 \text{ meV})\). At high temperatures or low cutoff frequencies, four of the five \( K_{\Delta(i,j,i',j')}(\omega) \) become negligible, and the surviving \( K_{-2}(\omega) \) approaches \( k_{\text{Marcus}}(\omega)/2J^2 \) (shown in purple).
prefactor does not make the entire expression exponentially small in $T$. In the high-temperature limit, the other four possibilities of $\Delta(i,j,i',j')$ give negligible results, as shown in fig. S1. Keeping only the $\Delta(i,j,i',j') = -2$ terms in eq. (S7) yields

$$R_{\nu\nu'} = 2J^2 A^4 \text{Re} [K_{-2}(\omega_{\nu\nu'})] \sum_{\langle i,j \rangle} \exp \left( -\frac{2(d_{i\nu} + d_{j\nu'})}{r_{\text{deloc}}} \right), \quad (S13)$$

where

$$K_{-2}(\omega) = \int_0^\infty d\tau e^{i\omega\tau} \left( e^{-2k_B T \tau^2 x_1} - e^{-4k_B T x_3} \right). \quad (S14)$$

This expression can be further simplified by neglecting the last term (which is small at high $T$), by noting that $2x_1 = \lambda$ (the definition of reorganisation energy), and by extending the lower limit of the integral to $-\infty$ (because the real part of the integrand is even) to give

$$\text{Re} [K_{-2}(\omega_{\nu\nu'})] = \frac{1}{2} \int_{-\infty}^\infty d\tau e^{i(\omega-\lambda)\tau} e^{-\lambda k_B T r^2} = \sqrt{\frac{\pi}{4\lambda k_B T}} \exp \left( -\frac{(\omega - \lambda)^2}{4\lambda k_B T} \right) = \frac{k_{\text{Marcus}}(\omega)}{2J^2}, \quad (S15)$$

where $k_{\text{Marcus}}$ is the Marcus hopping rate. Substituting this expression for $K_{-2}(\omega_{\nu\nu'})$ into eq. (S13) gives eq. (9) in the main text.

### S2. SIMPLIFIED JKMC RATE DERIVATION

The delocalisation correction $\xi_{\nu\nu'}$ for hopping between polarons $\nu$ and $\nu'$ can be simplified in the limit of low delocalisation to yield the simplified jKMC rate. As described in the main text,

$$\xi_{\nu\nu'} = A^4 \sum_{\langle i,j \rangle} \exp \left( -\frac{2(d_{i\nu} + d_{j\nu'})}{r_{\text{deloc}}} \right). \quad (S16)$$

For small $r_{\text{deloc}}$, the sum of exponentials in eq. (S16) is dominated by the terms that minimise the distance $d_{i\nu} + d_{j\nu'}$, where $i$ and $j$ are nearest neighbours. As shown in fig. S2, there are $d_{\nu\nu'}/a$ dominant terms with the minimal $d_{i\nu} + d_{j\nu'} = d_{\nu\nu'} - a$. Because $A = 1$ in the limit of localised charges, we obtain the simplified jKMC delocalisation correction

$$\xi_{\nu\nu'}^{\text{Simplified}} = \frac{d_{\nu\nu'}}{a} \exp \left( -\frac{2(d_{\nu\nu'} - a)}{r_{\text{deloc}}} \right). \quad (S17)$$

Figure S2. The arrangement of sites whose contribution dominates the jKMC rate. The dominant terms in the sPTRE minimise the distance $d_{i\nu} + d_{j\nu'}$ (shown in blue). On the cubic lattice, the simplest case is if the initial and final states $\nu$ and $\nu'$ lie in the same row (or column) of the lattice, as shown above. In that case, there are $d_{\nu\nu'}/a$ positions for the nearest-neighbours $i$ and $j$ which minimise this distance to $d_{\nu\nu'} - a$, and which occur when all four points are collinear. We use the same result ($d_{\nu\nu'}/a$ positions with total distance $d_{\nu\nu'} - a$) even if $\nu$ and $\nu'$ do not lie in the same row or column. This approximation is justified because the particular shape of the lattice is not an essential part of the jKMC model.
S3. SIMPLIFIED JKMC RESULTS

The mobility enhancements and times taken to reach the target energy $E_\mu$ for simplified jKMC are shown in fig. S3.

S4. EFFECTIVE IPR CONVERGENCE

Figure S4 shows that the lattices diagonalised in jKMC can be much smaller than those in dKMC. Smaller lattices are much easier to diagonalise, giving jKMC a significant computational advantage over dKMC.

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Figure S3. Simplified jKMC produces mobilities on the same order of magnitude as jKMC. In both (a) two and (b) three dimensions, simplified jKMC reproduces jKMC mobilities to about a factor of 2 (for the parameters tested), but tends to systematically overestimate them. Results are calculated for $\sigma = 150$ meV, $\lambda = 200$ meV, and $T = 300$ K. (c,d) The corresponding times taken to reach the target energy $E_\mu$ using simplified jKMC.
Figure S4. Calculations of effective IPRs at deep $\langle E \rangle$ converge rapidly as a function of lattice size. The effective IPR in $d$ dimensions is calculated using the neighbourhood-averaging method on a lattice of size $N_{box}^d$. (a) Calculations of the effective IPR converge when $N_{box}$ is large enough to accommodate the sizes of the delocalised polaron states that contribute to transport at $\langle E \rangle$. Here, $N_{box} \approx 20$ is sufficient for convergence for $\langle E \rangle$ below about $-300$ meV. By contrast, dKMC requires boxes large enough to converge the mean IPR of all states, corresponding to $\langle E \rangle = 0$, which would require substantially larger $N_{box}$. (b) Enlarged view of panel a for the values of $\langle E \rangle$ considered in this paper. Here, smaller $N_{box}$ suffice to achieve convergence because the effective IPR is a thermal average, mostly sensitive to low-energy, localised states that are adequately described using small lattices. Results are shown for three dimensions, $J = 75$ meV, $\sigma = 150$ meV, $\lambda = 200$ meV, and $T = 300$ K.