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Second-Quantized Surface Hopping

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The trajectory surface hopping method for quantum dynamics is reformulated in the space of many-particle states to include entanglement and correlation of trajectories. Used to describe many-body correlation effects in electronic structure theories, second quantization is applied to semiclassical trajectories. The new method allows coupling between individual trajectories via energy flow and common phase evolution. It captures the properties of a wave packet, such as branching, Heisenberg uncertainty, and decoherence. Applied to a superexchange process, the method shows very accurate results, comparable to exact quantum data and improving greatly on the standard approach.

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An accurate description of quantum dynamics is needed in many areas of physics and related disciplines, including photovoltaic and photocatalytic applications [1–3], light-operated nanoscale materials [4,5] and molecular electronics [6–9]. The large number of quantum, semiclassical, and quantum-classical techniques of varying complexity have been developed over the last few decades [10–15] and successfully applied to study nonequilibrium processes such as electron-phonon relaxation [1,16–18], charge and energy transfer [19,20], and photoinduced atomistic rearrangements [21,22]. Highly accurate fully quantum methods [23–25] are extremely computationally demanding and can be applied only to small systems and short time scales. Semiclassical schemes [26–28] are significantly more efficient and can be used with large systems. However, they provide only an approximate description and lack quantum effects, such as branching, uncertainty principle, zero-point energy, tunneling, and decoherence. Existing approaches that introduce these effects are either phenomenological [29,30] or mathematically and computationally involved [12,13,24,31–34]. Tully's fewest-switches surface hopping (FSSH) [26] is one of the most successful and widely used semiclassical methods, cited over 1000 times. The great popularity of the method can be attributed to its conceptual simplicity, acceptable accuracy, and high computational efficiency, which makes simulations of large systems feasible.

FSSH represents a quantum wave packet by a swarm of independent trajectories. This representation lacks intrinsically quantum effects. Some quantum effects can be introduced via phenomenological corrections, for example, by requiring the swarm of trajectories to have an initial spread in momenta and positions [26], or by mapping quantum variables on classical phase space [35]. Nonetheless, a swarm of decoupled classical trajectories does not properly represent a quantum-mechanical wave packet, in particular, since subsequent evolution does not allow energy exchange between the trajectories. Each trajectory conserves its energy in FSSH. To represent a wave packet, one needs to satisfy conservation of the total energy of the swarm, allowing energy exchange between individual trajectories. As a result, FSSH lacks quantum tunneling and is unable to describe closely related superexchange processes. Disentangled-trajectory approaches also lack decoherence effects. From the multiple trajectory point of view, decoherence arises because trajectories diverge and each trajectory acquires its own phase factor. Available from the simulation, this information is never utilized in FSSH. The lack of communication between evolving trajectories causes an excessive preservation of coherences, making FSSH overcoherent.

In this Letter, we report a new semiclassical method for description of quantum electron-phonon dynamics. Called second-quantized surface hopping (SQUASH), the method constructs a space of multitrajectory states and applies the FSSH technique in this space. The multitrajectory states are analogous to a many-particle basis in electronic structure theory. Obtained via second quantization, the many-particle basis is utilized to add correlation effects. SQUASH uses multitrajectory states to introduce correlation between trajectories via energy-based entanglement. The evolution of the quantum degrees of freedom for each trajectory is independent of all other trajectories; however, the surface hopping procedure performed in the multitrajectory basis entangles all trajectories and introduces intrinsically quantum effects, such as energy uncertainty, electronic decoherence, and tunneling. The SQUASH procedure requires conservation of the total energy of all entangled trajectories, but permits energy flow between individual trajectories, mimicking closely the properties of a quantum wave packet. The efficiency and utility of the approach is demonstrated with a superexchange process that is common to nanoscale and molecular systems. The proposed method is highly accurate and conceptually very simple. It provides a straightforward route to parallelization, facilitating its use for studies of large-scale systems.

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The time-dependent wave function ψ associated with an individual semiclassical trajectory is represented in terms of a quantum basis $|i\rangle$, which plays the role of 1-particle states:

$$\psi(1) = \sum_i c_i(1)|i\rangle. \tag{1}$$

Here, $c_i(t)$ are time-dependent expansion coefficients and (1) indicates that all quantities depend on properties of a single trajectory (particle number 1). The time evolution of the wave function coefficients is given by the standard semiclassical time-dependent Schrodinger equation (TDSE):

$$i\hbar\dot{c}_i(1) = \sum_j H_{ij}(1)c_j(1), \tag{2}$$

where $\hbar$ is the reduced Planck constant, the dot indicates the partial derivative with respect to time, and H is the Hamiltonian matrix. In a system comprised of electronic and nuclear degrees of freedom, the diagonal terms of the Hamiltonian contain the energies of electronic states E_i and kinetic energy of nuclei T:

$$H_{ij}(1) = [T(1) + E_i(1)]\delta_{ij} + (1 - \delta_{ij})V_{ij}. \tag{3}$$

The off-diagonal elements V_{ij} may contain only electronic couplings (diabatic basis), or only nonadiabatic couplings (adiabatic basis), or both (arbitrary basis). For notation simplicity, we use the diabatic representation. Generalization to an arbitrary basis is straightforward.

The choice of a particular representation is motivated by physical and computational considerations. The accuracy of the FSSH is generally higher in the adiabatic representation, which is commonly available in the standard electronic structure calculations. However, the adiabatic representation fails in many situations. It causes insurmountable numerical problems in extended systems, because nonadiabatic couplings between states located within distant subsystems increase to infinity in avoided crossing regions [36]. The adiabatic representation cannot describe the physics of transition from coherent to hopping transport in long-range charge and energy transfer [37]. Diabatic representations are much more reliable and give better results in such cases.

The use of a diabatic basis is encouraged by the fragment-based or multiconfiguration electronic structure methods, including the valence bond and constrained density functional theories. Diabatic states are readily available in these approaches, even in large systems. They are associated with different exciton and charge localization states in biological and nanoscale materials, and reactants and products in reactive systems.

The diabatic representation is chosen in this work to illustrate the superexchange mechanism, which is common to many physical processes mediated by high-energy intermediate states. The mechanism is best understood in the diabatic picture. Superexchange is possible between adiabatic states as well. For instance, the initial and final adiabatic electronic states in Raman-type processes are coupled to a high-energy intermediate adiabatic state by electromagnetic field. The advantages of the developed approach apply to both diabatic and adiabatic representations.

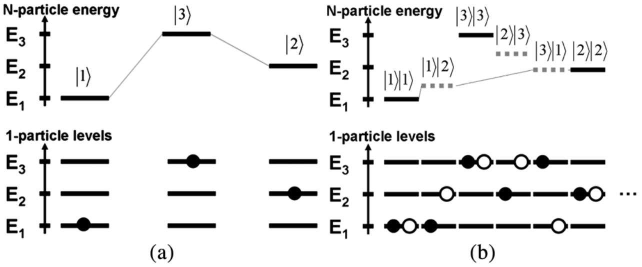

FIG. 1. Construction of N-particle states from 1-particle states for a 3-level system. (a) 1-particle state basis used in the FSSH method; (b) 6 of 9 possible 2-particle states. All particles are distinguishable. N-particle state energies are normalized to the number of particles. Each energy level can be occupied by any number particles from 0 to N, provided that the total number of particles distributed in all levels is N. Additional lower-energy levels are created between the original states $|1\rangle$ and $|2\rangle$. Utilizing only the 2-particle states denoted by black lines in the top section of part (b) is equivalent to the 1-particle FSSH scheme of panel (a).

We consider the basis of N-particle states, $|I_N\rangle = |i_1\rangle|i_2\rangle\cdots|i_N\rangle$ (Fig. 1). The N-particle wave function can be written as

$$\begin{aligned}\Psi(1,2,\ldots,N) &= \sum_I C_I(1,2,\ldots,N)|I_N\rangle \\ &= \sum_{i_1,i_2,\ldots,i_N} c_{i_1}(1)c_{i_2}(2)\ldots c_{i_N}(N)|i_1\rangle|i_2\rangle\ldots|i_N\rangle.\end{aligned} \tag{4}$$

The sum in Eq. (4) includes M^N distinct N-particle states and corresponding N-particle coefficients, $C_I(1,2,\ldots,N) = c_{i_1}(1)c_{i_2}(2)\ldots c_{i_N}(N)$, where M is the number of 1-particle states. According to its definition, the time evolution of the N-particle coefficient is given by

$$\begin{aligned}i\hbar\dot{C}_I(1,2,\ldots,N) &= i\hbar\sum_{k=1}^{N}\dot{c}_{i_k}(k)\prod_{\substack{n=1 \\ n\neq k}}^{N} c_{i_n}(n) \\ &= \sum_{k=1}^{N}\sum_j H_{i_k j}(k)\left[c_j(k)\prod_{\substack{n=1 \\ n\neq k}}^{N} c_{i_n}(n)\right] \\ &= \sum_{J=1}^{M^N} H_{IJ}(1,2,\ldots,N)C_J(1,2,\ldots,N).\end{aligned} \tag{5}$$

Equation (5) is an N-particle analog of the 1-particle Eq. (2). The solution of Eq. (5) is equivalent to solution of N Eqs. (2). Therefore, one does not need to propagate N-particle coefficients by directly solving Eq. (5). Instead, one solves N independent TDSEs one at a time. The main result that Eq. (5) conveys is the definition of the energies of N-particle states and the couplings between them. As intuitively expected, the energy (either potential or kinetic) of an N-particle state in this model is given by the sum of the corresponding 1-particle energies. The structure of the coupling matrix between many-particle states is less trivial, and can be obtained explicitly by considering the mapping, Eq. (5).

Starting with Eq. (5), and following the term separation procedure similar to the one performed in the derivation of the original 1-particle FSSH [26], one can obtain the expression for the hopping probabilities between many-particle states. The expression is formally identical to the one in FSSH, and only requires an explicit definition of the N-particle coefficients, $C_J(1,2,\ldots,N)$, and the N-particle Hamiltonian matrix elements $H_{IJ}(1,2,\ldots,N)$. The SQUASH method modifies the velocity rescaling procedure, as explained below. The rest of the SH algorithm remains the same as in the original FSSH.

The velocity rescaling procedure in SQUASH mimics wave packet energy conservation in quantum mechanics: The rescaling does not enforce energy conservation for each 1-particle trajectory. Rather, one considers the total energy of the N-particle ensemble. The sum of the kinetic and potential energies of the initial and final states T_I, E_I and T_F, E_F is conserved:

$$T_I + E_I = T_F + E_F. \tag{6}$$

The transition to final state $|F\rangle$ is allowed only when $T_F = T_I + E_I - E_F \geq 0$. The resulting kinetic energy of the N-particle state $|F\rangle$ is given by the sum of kinetic energies of N 1-particle trajectories:

$$T_F = \sum_{i=1}^{N} \frac{p^2(i)}{2m}. \tag{7}$$

The N 1-particle momenta that satisfy Eq. (7) form an N-dimensional hypersphere. Any point on this hypersphere satisfies the energy conservation law, Eq. (6). In the 1-particle FSSH, the momentum variable for each individual trajectory is restricted to only 2 allowed values—the end points of a one-dimensional sphere (line) of a smaller radius (Fig. 2).

In the N-dimensional case, the choice of points on the hypersphere is more flexible. The hypersphere is reduced to a circle for the 2-particle basis (Fig. 2). We define momenta of each of the two 1-particle trajectories by

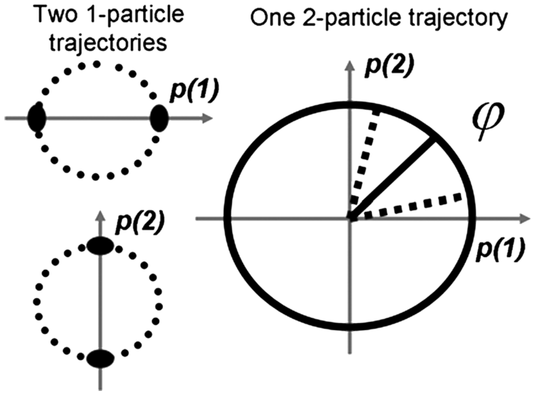

FIG. 2. Possible values of nuclear momenta in the rescaling scheme in the case of two disentangled 1-particle trajectories (as in FSSH) and one 2-particle trajectory (SQUASH).

$$p(1) = P\cos\left(\phi\frac{\pi}{2}\right), \tag{8a}$$

$$p(2) = P\sin\left(\phi\frac{\pi}{2}\right), \tag{8b}$$

where P is the magnitude of the total momentum, determined from the energy conservation, Eq. (6), and $\phi(\pi/2)$ is the angle that determines the redistribution of momenta among the two coupled trajectories. In the present scheme, the parameter ϕ is set to $\frac{1}{2}$ (solid line in Fig. 2) corresponding to uniform scaling of the momenta of the two trajectories.

The rescaled momenta, Eq. (8), can be generalized in a multidimensional case to control kinetic energy redistribution among coupled individual trajectories. For example, it is known that the classical limit of the momentum change corresponds to rescaling in the direction of the derivative coupling vectors [38]. The coupling of individual trajectories realized via energy redistribution can lead to nonuniform or random scaling of the *absolute values* of the momenta, while complying with the classical limit of the scaling direction. The SQUASH theory allows for more general prescriptions. The choice of the most accurate velocity-rescaling scheme requires further studies. In particular, we intend on investigating the quantum jump schemes appearing in the quantum-classical formulations based on the partial Wigner transform formalism [12,39].

To illustrate the accuracy of the SQUASH method, we study the superexchange process in the 3-state model of Wang *et al.* [40]. The model is motivated by Auger and multiple exciton generation processes in nanoscale materials [41–43] and singlet fission in organic photovoltaics, which proceed via intermediate states [44]. The superexchange mechanism is also common in conductivity and molecular electronics [6,7,9]. In superexchange, a quantum transition between the initial and final states involves intermediate states of higher energy. The intermediate

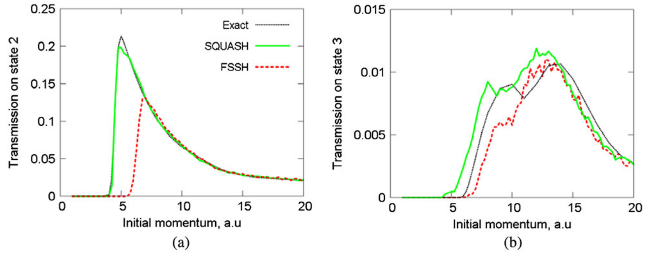

FIG. 3 (color online). Probabilities of transmission on the (a) second and (b) third states. Performance of three methods is compared: FSSH, exact quantum solution, and SQUASH with 2-particle states. SQUASH describes the superexchange transmission mechanism corresponding to the initial momenta around 5 a.u., part (a), while FSSH does not allow superexchange.

states never gain significant population and provide coupling between the initial and final states.

The model consists of 3 states, with the energy alignment corresponding to Fig. 1(a). The direct coupling between states 1 and 2 set to zero. The Hamiltonian is defined by $E_1(x) = 0$, $E_2(x) = 0.005$, $E_3(x) = 0.01$, $V_{12}(x) = V_{21}(x) = 0$, $V_{13}(x) = V_{31}(x) = 0.001 \exp(-x^2/2)$, $V_{23}(x) = V_{32}(x) = 0.01 \exp(-x^2/2)$. The atomic units of length and energy are used. The mass of the particle is set to 2000 a.u. The initial momenta of the trajectories are sampled from the normal distribution centered at the mean value. The spread of the distribution is 20% of the mean value. Equations of motion for the electronic and nuclear degrees of freedom are integrated using the 4th order Runge-Kutta method with the time step of 0.1 fs, until the trajectory leaves the coupling region. When performing N-particle simulations, the final populations of N-particle states are projected onto the 1-particle states. For example, if the 2-particle trajectory ends up in the state $|1\rangle|3\rangle$, $1/2$ is added to the count of the 1-particle state $|1\rangle$ and $1/2$ is added to the count of the 1-particle state $|3\rangle$ for each stochastic realization of the surface hopping algorithm.

The 1-particle formulation of SQUASH is equivalent to the original FSSH scheme. Nontrivial effects appear starting from the 2-particle trajectories. The scattering probabilities computed in the basis of 2-particle states (9 states in the 3-level system) are shown in Fig. 3. We show only the probabilities of transmission on states 2 and 3, because the reflection probabilities are zero [40]. The probability of transmission on state 1 can be inferred from the data in Fig. 3. The performance of the new method is compared with that of the standard FSSH and exact quantum results.

The transition probability on state 2 directly characterizes the degree to which the superexchange effect is accounted for by different methods. The SQUASH method produces very accurate scattering probabilities—much closer to the exact solution than FSSH, especially in the region of low initial nuclear kinetic energy. The superexchange process for small initial momenta is possible in SQUASH due to energy exchange between semiclassical trajectories in the many-particle basis. In FSSH, one encounters situations when the kinetic energy of each of the two trajectories is insufficient to overcome the energy barrier associated with state 3. In the entangled description, the energy of one trajectory can be transferred to the other one. The energy-donor trajectory cannot hop, but the energy-acceptor trajectory can. This simple scheme presents new physics behind surface hopping, and reflects the quantum nature of wave packets. Thus, the SQUASH formulation of trajectory surface hopping not only is more accurate than FSSH, but also captures essential properties of quantum dynamics in general, and superexchange in particular.

To recapitulate, we have presented the new semiclassical method for quantum dynamics. The method uses a second-quantization representation of surface hopping, motivating the name, SQUASH. It utilizes many-particle states for performing surface hopping. By relaxing energy conservation for individual trajectories, and requiring the conservation at the multitrajectory level, SQUASH entangles individual trajectories and represents faithfully the evolution of a quantum wave packet. At the single particle level, SQUASH is equivalent to the extremely popular FSSH semiclassical technique. Already at the 2-particle level, SQUASH provides significant improvement at both quantitative and qualitative levels, as demonstrated with a model representing the superexchange mechanism of quantum transitions. The new approach maintains the conceptual simplicity of surface hopping, introduces new physics, and captures essential quantum phenomena, such as wave packet splitting, the uncertainty principle, and decoherence. The method is conceptually simple and computationally efficient. It can be parallelized easily, to provide a further boost in efficiency and allowing applications to large systems.

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[1] S. V. Kilina, A. J. Neukirch, B. F. Habenicht, D. S. Kilin, and O. V. Prezhdo, Phys. Rev. Lett. **110**, 180404 (2013).
[2] C. Creatore, M. Parker, S. Emmott, and A. Chin, Phys. Rev. Lett. **111**, 253601 (2013).
[3] K. R. Harikumar, J. C. Polanyi, A. Zabet-Khosousi, P. Czekala, H. Lin, and W. A. Hofer, Nat. Chem. **3**, 400 (2011).
[4] Y. Nabetani, H. Takamura, Y. Hayasaka, T. Shimada, S. Takagi, H. Tachibana, D. Masui, Z. Tong, and H. Inoue, J. Am. Chem. Soc. **133**, 17130 (2011).
[5] W. A. Velema, W. Szymanski, and B. L. Feringa, J. Am. Chem. Soc. **136**, 2178 (2014).

[6] N. Zhitenev, H. Meng, and Z. Bao, Phys. Rev. Lett. **88**, 226801 (2002).

[7] ž. Crljen and G. Baranović, Phys. Rev. Lett. **98**, 116801 (2007).

[8] S. Gustavsson, R. Leturcq, M. Studer, T. Ihn, K. Ensslin, D. C. Driscoll, and A. C. Gossard, Nano Lett. **8**, 2547 (2008).

[9] Y. Kim, A. Garcia-Lekue, D. Sysoiev, T. Frederiksen, U. Groth, and E. Scheer, Phys. Rev. Lett. **109**, 226801 (2012).

[10] G. Stock and M. Thoss, Phys. Rev. Lett. **78**, 578 (1997).

[11] J. C. Tully, Faraday Discuss. **110**, 407 (1998).

[12] R. Kapral and G. Ciccotti, J. Chem. Phys. **110**, 8919 (1999).

[13] A. Donoso and C. Martens, Phys. Rev. Lett. **87**, 223202 (2001).

[14] C. Craig, W. Duncan, and O. Prezhdo, Phys. Rev. Lett. **95**, 163001 (2005).

[15] A. V. Akimov, A. J. Neukirch, and O. V. Prezhdo, Chem. Rev. **113**, 4496 (2013).

[16] B. Habenicht, C. Craig, and O. Prezhdo, Phys. Rev. Lett. **96**, 187401 (2006).

[17] B. Habenicht and O. Prezhdo, Phys. Rev. Lett. **100**, 197402 (2008).

[18] A. J. Neukirch, K. Hyeon-Deuk, and O. V. Prezhdo, Coord. Chem. Rev. **263–264**, 161 (2014).

[19] T. Nelson, S. Fernandez-Alberti, A. E. Roitberg, and S. Tretiak, Acc. Chem. Res. **47**, 1155 (2014).

[20] N. Martsinovich and A. Troisi, Energy Environ. Sci. **4**, 4473 (2011).

[21] J. Clark, T. Nelson, S. Tretiak, G. Cirmi, and G. Lanzani, Nat. Phys. **8**, 225 (2012).

[22] T. S. Kuhlman, W. J. Glover, T. Mori, K. B. Møller, and T. J. Martínez, Faraday Discuss. **157**, 193 (2012).

[23] M. Ben-Nun and T. J. Martínez, J. Chem. Phys. **108**, 7244 (1998).

[24] M. Ben-Nun, J. Quenneville, and T. J. Martínez, J. Phys. Chem. A **104**, 5161 (2000).

[25] M. H. Beck, A. Jackle, G. A. Worth, and H.-D. Meyer, Phys. Rep. **324**, 1 (2000).

[26] J. C. Tully, J. Chem. Phys. **93**, 1061 (1990).

[27] G. Käb, Phys. Rev. E **66**, 046117 (2002).

[28] X. Li, J. C. Tully, H. B. Schlegel, and M. J. Frisch, J. Chem. Phys. **123**, 084106 (2005).

[29] B. J. Schwartz, E. R. Bittner, O. V. Prezhdo, and P. J. Rossky, J. Chem. Phys. **104**, 5942 (1996).

[30] H. M. Jaeger, S. Fischer, and O. V. Prezhdo, J. Chem. Phys. **137**, 22A545 (2012).

[31] C. C. Martens and J.-Y. Fang, J. Chem. Phys. **106**, 4918 (1997).

[32] E. Roman and C. C. Martens, J. Phys. Chem. A **111**, 10256 (2007).

[33] S. Bonella, G. Ciccotti, and R. Kapral, Chem. Phys. Lett. **484**, 399 (2010).

[34] S. Nielsen, R. Kapral, and G. Ciccotti, J. Stat. Phys. **101**, 225 (2000).

[35] X. Sun and W. H. Miller, J. Chem. Phys. **106**, 6346 (1997).

[36] L. Wang and O. V. Prezhdo, J. Phys. Chem. Lett. **5**, 713 (2014).

[37] L. Wang and D. Beljonne, J. Phys. Chem. Lett. **4**, 1888 (2013).

[38] D. F. Coker and L. Xiao, J. Chem. Phys. **102**, 496 (1995).

[39] O. V. Prezhdo and V. V. Kisil, Phys. Rev. A **56**, 162 (1997).

[40] L. Wang, D. Trivedi, and O. V. Prezhdo, J. Chem. Theory Comput. **10**, 3598 (2014).

[41] S. Konabe and S. Okada, Phys. Rev. Lett. **108**, 227401 (2012).

[42] J. Iveland, L. Martinelli, J. Peretti, J. S. Speck, and C. Weisbuch, Phys. Rev. Lett. **110**, 177406 (2013).

[43] S. Wippermann, M. Vörös, D. Rocca, A. Gali, G. Zimanyi, and G. Galli, Phys. Rev. Lett. **110**, 046804 (2013).

[44] A. V. Akimov and O. V. Prezhdo, J. Am. Chem. Soc. **136**, 1599 (2014).