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Quantum Backreaction through the Bohmian Particle

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A novel solution to the quantum backreaction problem in a mixed quantum-classical simulation is provided using the Bohmian interpretation of quantum mechanics. The Bohmian backreaction is unique, computationally simple, features reaction channel branching, and easily gives the full classical limit. The Bohmian quantum-classical method is illustrated by application to a model of O_2 interacting with a Pt surface.

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Quantum mechanics describes the majority of physical phenomena in nature; however, numerous instances are known where mixed quantum-classical models are needed. On one hand, complex many-body dynamics of chemical reactions are rarely amenable to a fully quantum-mechanical treatment. Mixed quantum-classical models that treat the light particles such as electrons and protons quantum mechanically and the heavy particles such as atomic nuclei classically provide tremendous computational advantages over fully quantum-mechanical models. On the other hand, there exist classical theories such as the theory of gravity, where quantum counterparts have not yet been fully established. The problem of coupling quantum and classical degrees of freedom raises controversial issues which, apparently, do not admit a unique solution. Numerous coupling schemes have been proposed ranging from the formal mathematical solutions [1–13] to the specific algorithms that have been applied to various problems in chemical physics [14–34]. The effect of the classical degrees of freedom on the evolution of the quantum variables is straightforward. Typically, the quantum particles are considered in the presence of a time-dependent potential generated by the moving classical particles. The difficulties in the coupling of quantum and classical mechanics lie in the definition of the quantum backreaction on the classical degrees of freedom. The most straightforward and yet rigorous approach is based on the Ehrenfest theorem and leads to the mean-field (MF) approximation where classical particles evolve in the MF of the quantum wave function. Unfortunately, MF trajectories do not branch as do quantum wave packets. The branching of trajectories towards different reaction channels is typically achieved by multiconfiguration MF approaches [1,22,35,36], by surface hopping (SH) procedures [19–22,25,26,28–30,37], or via decoherence [1,10,11,32]. The decoherence based approach [32] to trajectory branching relies on quantum properties of the "classical" subsystem [10,11] and, therefore, is not a truly quantum-classical method. Multiconfiguration MF (MMF) [1,22,35,36], the velocity coupling approximations (VCA) of Ref. [38], and SH [19–22,25,26,28–30,37] are bona fide quantum-classical approaches. However, MMF requires a careful selection of the configuration basis for each system. Both MMF and the VCA schemes generate ensembles of *coupled* classical trajectories significantly increasing the computational effort. SH generates one trajectory at a time, but is *ad hoc* and varies substantially from one implementation to another [19–22,25,26,28–30,37].

In this Letter we propose a solution to the quantum backreaction problem based on the de Broglie–Bohm or hydrodynamic interpretation of quantum mechanics [39–42], which has experienced increased popularity, drawing both epistemological [43] and practical [44–46] interest. The proposed Bohmian backreaction is unique, is computationally simple, and describes a truly quantum-classical case. Similar to classical mechanics, Bohmian quantum mechanics deals with particles and particle trajectories. Each quantum degree of freedom is represented by an ensemble of coupled particles. If, according to our proposal, a classical particle is coupled to a single member of the quantum Bohmian ensemble, an ensemble of classical trajectories capable of branching is generated, in contrast to the MF situation in which a single average trajectory exists. In contrast to the MMF and VCA methods, classical trajectories in the generated ensemble are not coupled and are obtained one at a time. The MF trajectory can be recovered from the generated ensemble by the averaging. The Bohmian quantum-classical approach differs from the family of *ad hoc* SH methods by providing a unique prescription for the correlation between the classical trajectories and the ensemble of quantum ones. In contrast to the decoherence based stochastic MF method [32] that relies on quantum properties of the heavy particles, the Bohmian mechanics leads to a truly quantum-classical description where only classical positions and momenta of the heavy particles are involved. Unique to the Bohmian quantum-classical mechanics, fully classical dynamics for all degrees of freedom is straightforwardly recovered by setting $\hbar$ to 0. The fully classical limit is not trivial to obtain in the other approaches, but is particularly useful in the cases when the quantum contribution to the dynamics is important only for a short time [45,46]. After an initial period of quantum dynamics in such cases, the classical limit provides the exact answer. The quantum-classical Bohmian dynamics can fully exploit this phenomenon.

Note that a related paper [47] dealing with mixing quantum and classical mechanics using Bohmian trajectories has appeared while this one was being reviewed. Our approach was developed independently and results in different equations than that of Ref. [47]. In particular, in contrast to Eq. (17) of Ref. [47], our Eq. (9) for the quantum force is simpler containing only the derivative of the ordinary potential V and not the quantum one Q, following the time-dependent Hellmann-Feynman theorem [22,48]. Importantly, our derivation starts from the most straightforward quantum-classical approximation, the mean-field one, and obtains the Bohmian quantum-classical method in a single step by moving the quantum-mechanical averaging from dynamics to initial conditions. Thus, a connection to the existing quantum-classical methods is established. The goal of the present Letter is not to suggest another quantum-classical approach, but to propose a unique solution to the quantum backreaction problem [5–9,11].

Consider a mixed quantum (x)–classical (X) system, where the quantum Hamiltonian $H(x;X)$ depends parametrically on the positions of classical particles

$$H(x;X) = -\frac{\hbar^2}{2m}\nabla_x^2 + V(x;X). \tag{1}$$

The total energy of the quantum-classical system is the sum of the quantum Hamiltonian expectation value with the classical kinetic and potential $W(X)$ energies

$$\begin{aligned} E^{\mathrm{tot}} &= E^{\mathrm{quant}} + E^{\mathrm{cl}} \\ &= \int d^3x\, \Psi^*(x) H(x;X) \Psi(x) + \frac{M\dot{X}^2}{2} + W(X). \end{aligned} \tag{2}$$

The wave function $\Psi(x)$ evolves according to the time-dependent Schrödinger equation

$$i\hbar\frac{\partial\Psi(x)}{\partial t} = \left(-\frac{\hbar^2}{2m}\nabla_x^2 + V\big(x;X(t)\big)\right)\Psi(x), \tag{3}$$

where the potential V is time dependent through dynamics of classical variables $X(t)$. The evolution of the classical coordinates obeys the Newton equation

$$M\ddot{X} = -\nabla_X W(X) + F^{\mathrm{quant}} \tag{4}$$

which, in addition to the ordinary classical force $-\nabla_X W(X)$, contains the quantum force F^{quant}. The definition of the quantum force constitutes the *quantum backreaction problem.* The quantum force of the mean-field approach is the average of the gradient of the quantum Hamiltonian

$$F^{\mathrm{quant}} = -\int d^3x\, \Psi^*(x)\,[\nabla_X H(x;X)]\Psi(x). \tag{5}$$

The mean-field force conserves the total quantum-classical energy (2) as established by the time-dependent version of the Hellmann-Feynman theorem [22,48].

Next, consider how the energy conserving mean-field force is formulated in Bohmian mechanics. de Broglie [39,40] and Bohm [41,42] express the wave function in the polar form $\Psi(x) = R(x)\exp[iS(x)/\hbar]$ and rewrite the expectation value of the quantum Hamiltonian as

$$\int d^3x\, \Psi^*(x)\left[-\frac{\hbar^2}{2m}\nabla_x^2 + V(x;X)\right]\Psi(x) = \int d^3x\, R^2(x)\left[\frac{(\nabla_x S(x))^2}{2m} + Q(x) + V(x;X)\right], \tag{6}$$

where $Q(x)$ is the "quantum potential"

$$Q(x) = -\frac{\hbar^2}{2m}\frac{\nabla_x^2 R(x)}{R(x)}. \tag{7}$$

Since $R^2(x) = \Psi^*(x)\Psi(x)$ is the quantum probability distribution, the quantum energy (6) is interpreted in Bohmian mechanics as the energy of an ensemble of particles, each one with the energy $[(\nabla_x S(x))^2/2m + Q(x) + V(x;X)]$ and the probability distribution $R^2(x)$. The mean-field quantum force in the de Broglie–Bohm interpretation takes the following form:

$$F^{\mathrm{quant}} = -\int d^3x\, R^2(x)\nabla_X V(x;X) \tag{8}$$

and can be viewed as the average of the forces $-\nabla_X \times V(x;X)$ due to an ensemble of Bohmian particles with the probability distribution $R^2(x)$. The ensemble averaged Bohmian force (8) is identical to the ordinary mean-field force (5), since by the time-dependent Hellmann-Feynman theorem [22,48] the time derivative of the expectation value of the quantum energy involves only the derivative of the quantum Hamiltonian and not of the wave function $\Psi(x)$ and, therefore, not of $R^2(x)$, $S(x)$, or $Q(x)$. As before, the ensemble averaged force now given by Eq. (8) conserves the total quantum-classical energy, Eq. (2).

The solution to the quantum backreaction problem proposed here moves the $R^2(x)$ ensemble averaging outside quantum-classical dynamics. The averaging is performed only once at the final time. The quantum force does not involve the averaging but is calculated for a single representative of the Bohmian ensemble. The simulation runs by the following algorithm. *First*, initial conditions for the wave function and the classical trajectory are chosen in the usual manner. Positions x of Bohmian particles are sampled from the initial distribution $R^2(x)$. An ensemble of quantum-classical systems is generated each with a different initial position of the Bohmian particle, but the same initial conditions for the wave function and the heavy particle. *Second*, for each member of the quantum-classical ensemble the wave function is propagated by the time-dependent Schrödinger equation (3). The classical trajectory evolves by the Newton equation (4) with the quantum force

$$F^{\text{quant}} = -\nabla_X V(x;X), \tag{9}$$

which depends on the position of the Bohmian particle x. The trajectory of the Bohmian particle is propagated [43–46] by

$$m\ddot{x} = -\nabla_x[Q(x) + V(x;X)] \tag{10}$$

or, equivalently, by $\dot{x} = \nabla_x S/m$. *Third*, the results are averaged over the Bohmian ensemble. Since the wave function remains a solution to the time-dependent Schrödinger equation, the Hellmann-Feynman theorem still applies. In order to conserve the total energy, the quantum energy must be calculated by Eq. (6) with the entire distribution function $R^2(x)$. In practice this means that all trajectories of the heavy particle originating from the Bohmian ensemble $R^2(x)$ must be considered. The Bohmian quantum-classical method is defined by Eqs. (3), (4), (9), and (10). The fully classical limit for both x and X is easily achieved by setting $\hbar \to 0$.

We illustrate the Bohmian backreaction method with the model intended as a simplified representation of gaseous oxygen interacting with a platinum surface, Ref. [21]. The model consists of a light particle x with mass m colliding with a heavier particle X with mass M. The heavy particle is bound to an immobile surface. The total Hamiltonian for the system is given by

$$\begin{aligned} H(x;X) = T_x + T_X + V_x(x) + V_X(X) \\ + V_{xX}(x;X), \end{aligned} \tag{11}$$

$$\text{with } V_X(X) = \frac{1}{2}M\Omega^2X^2, \tag{12}$$

$$V_x(x) = a[e^{-2b(x-c)} - 2e^{-b(x-c)}], \tag{13}$$

$$V_{xX}(x;X) = Ae^{-B(x-X)}, \tag{14}$$

where T_x and T_X are the kinetic energy operators. The harmonic potential V_X describes the interaction of the heavy particle with the surface. The Morse potential V_x describes the interaction of the lighter particle with the surface. The two particles interact by the exponentially repulsive potential V_{xX}. Parameters particular to the simulation are provided in Table I and are the same as in Ref. [21]. Initially, the light particle is moving towards the heavy particle. The initial conditions of the heavy particle are sampled microcanonically to represent the ground state of the harmonic oscillator. The light particle is described by a Gaussian wave packet

$$\Psi(x, t = 0) = \exp\left[\frac{ik_0x}{\hbar}\right]\exp\left[-\frac{(x - x_0)^2}{\gamma^2}\right] \tag{15}$$

located 6 Å away from the surface with the initial momentum $k_0 = -\sqrt{2E_0/m}$ corresponding to the incident energy E_0. The results of the simulation are characterized by the light particle scattering probability as a function of time

$$P_s(t) = \int_{x_s}^{\infty} |\Psi(x,t)|^2\, dx \tag{16}$$

with $x_s \approx 5.8$ Å. The time-dependent net scattering probability obtained via the Bohmian quantum-classical technique is averaged over 1500 trajectories and is judged in Fig. 1 relative to the fully quantum solution and the MF dynamics.

The Bohmian approach correctly reproduces the asymptotic value of the scattering probability in sharp contrast to the MF data. As discussed in Ref. [21], the failure of the MF method to reproduce the complete scattering of the wave packet stems from the average nature of the MF quantum backreaction. The light particle wave packet splits and a part of it remains temporarily trapped with the heavy particle. In the exact solution the trapped part of the wave packet follows the scattered part and eventually decays. The two parts of the light particle wave packet become correlated with different parts of the heavy particle wave packet. A single MF trajectory of the heavy particle cannot describe this correlation. As a result, the energy exchange between the light and the heavy particles is treated incorrectly by MF, and the trapped part of the light particle

TABLE I. Numerical parameters used in simulation of the scattering problem.

m	1 amu	a	700 kJ/mol
M	10 amu	b	5.0 Å^{-1}
Ω	5×10^{14} s^{-1}	c	0.7
A	10^4 kJ/mol	x_0	6.0 Å
B	4.25 Å^{-1}	γ	0.5 Å

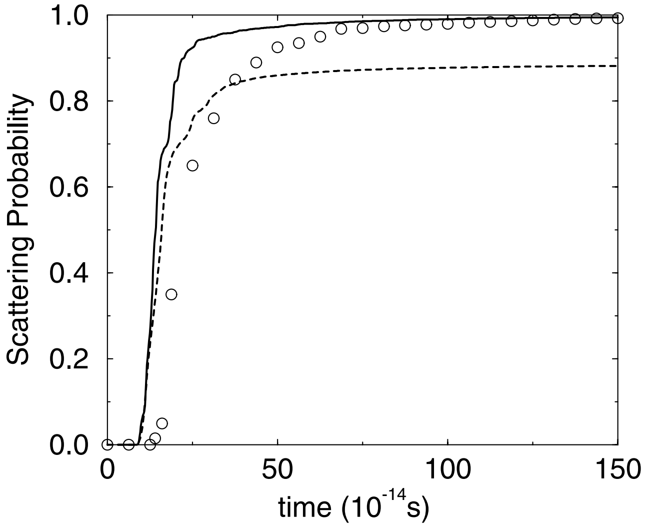

FIG. 1. The time-dependent scattering probability P_s, Eq. (16), for the model problem detailed in the text obtained for the incident energy of 20 kJ/mol using exact quantum dynamics (circles), mean-field dynamics (dashed curve), and the Bohmian quantum-classical technique (solid curve).

never decays [21]. In the quantum-classical Bohmian approach, the backreactions of the scattered and transiently trapped parts of the light particle onto the heavy one are not averaged, but independent. An ensemble of heavy particle trajectories is generated and gives the right asymptotic behavior.

The Bohmian approach to the coupling of quantum and classical mechanics provides another opportunity for quantum-classical coupling that is not attainable previously by the traditional MF and SH approaches. Consider a situation such as in Ref. [37], where a molecular complex AH-B is coupled to a solvent. The proton H has to be treated quantum mechanically, while both A and B atoms and the solvent can be treated classically. In the traditional approaches the quantum-classical coupling of the proton to solvent is formulated in exactly the same way as its coupling to the atoms A and B. If the proton tunnels between A and B, but does not tunnel into the solvent, the quantum behavior of the proton depends only on the interaction with A and B. In the Bohmian quantum-classical method it is then conceivable to couple the proton to A and B quantum mechanically and to the solvent classically. The evolution of the proton will be determined by the ordinary V and quantum Q potentials, Eq. (10). The V potential will contain both the proton-A,B and proton-solvent coupling terms, while the time-dependent Schrödinger equation that determines the Q potential will be decoupled from the solvent and will depend only on A and B. In order to couple the quantum-mechanical proton to the classical solvent, the traditional methods must include the solvent dependent terms in the Schrödinger equation for the proton. The Bohmian quantum-classical approach can provide significant savings by ignoring the multiple solvent terms in the Schrödinger equation, but including the solvent terms into the Newton equation (10) for the proton.

To recapitulate, we have presented a novel solution to the quantum backreaction problem in a mixed quantum-classical simulation. It is given within the Bohmian interpretation of quantum mechanics. The Bohmian backreaction is uniquely defined and computationally simple. It features trajectory branching into reaction channels and provides straightforward connection to the full classical limit.

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[1] O. V. Prezhdo and V. V. Kisil, Phys. Rev. A **56**, 162 (1997).
[2] J. Caro and L. L. Salcedo, Phys. Rev. A **60**, 842 (1999).
[3] I. V. Aleksandrov, Z. Naturforsch. **36A**, 902 (1981).
[4] W. Boucher and J. Traschen, Phys. Rev. D **37**, 3522 (1988).
[5] A. Anderson, Phys. Rev. Lett. **74**, 621 (1995).
[6] K. R. W. Jones, Phys. Rev. Lett. **76**, 4087 (1996).
[7] L. Diósi, Phys. Rev. Lett. **76**, 4088 (1996).
[8] I. R. Senitzky, Phys. Rev. Lett. **76**, 4089 (1996).
[9] A. Anderson, Phys. Rev. Lett. **76**, 4090 (1996).
[10] J. J. Halliwell, Phys. Rev. D **57**, 2337 (1998).
[11] L. Diósi and J. J. Halliwell, Phys. Rev. Lett. **81**, 2846 (1998).
[12] V. V. Kisil, Phys. Essays **11**, 69 (1998).
[13] K. Hepp, Commun. Math. Phys. **35**, 265 (1974).
[14] A. D. McLachlan, R. D. Gregory, and M. A. Ball, Mol. Phys. **7**, 119 (1963–1964).
[15] P. Pechukas, Phys. Rev. **181**, 174 (1969).
[16] E. E. Nikitin, *Theory of Elementary Atomic and Molecular Processes in Gases* (Clarendon, Oxford, 1974).
[17] W. H. Miller and T. F. George, J. Chem. Phys. **56**, 5637 (1972).
[18] X. Sun and W. H. Miller, J. Chem. Phys. **106**, 916 (1997).
[19] J. C. Tully and R. K. Preston, J. Chem. Phys. **55**, 562 (1971).
[20] J. C. Tully, J. Chem. Phys. **93**, 1061 (1990).
[21] D. S. Sholl and J. C. Tully, J. Chem. Phys. **109**, 7702 (1998).
[22] J. C. Tully, in *Classical and Quantum Dynamics in Condensed Phase Simulations,* edited by B. J. Berne, G. Ciccotti, and D. F. Coker (World Scientific, Singapore, 1998), pp. 489–514.
[23] E. J. Heller, J. Chem. Phys. **62**, 1544 (1975).
[24] R. B. Gerber, V. Buch, and M. A. Ratner, J. Chem. Phys. **77**, 3022 (1982).
[25] N. C. Blais and D. G. Truhlar, J. Chem. Phys. **79**, 1334 (1983).
[26] M. F. Herman, Annu. Rev. Phys. Chem. **45**, 83 (1994).
[27] G. D. Billing, Int. Rev. Phys. Chem. **13**, 309 (1994).

[28] F. A. Webster, P. J. Rossky, and R. A. Friesner, Comput. Phys. Commun. **63**, 494 (1991).

[29] E. R. Bittner and P. J. Rossky, J. Chem. Phys. **103**, 8130 (1995).

[30] O. V. Prezhdo and P. J. Rossky, J. Chem. Phys. **107**, 825 (1997).

[31] O. V. Prezhdo and P. J. Rossky, Phys. Rev. Lett. **81**, 5294 (1998).

[32] O. V. Prezhdo, J. Chem. Phys. **111**, 8366 (1999).

[33] O. V. Prezhdo, Phys. Rev. Lett. **85**, 4413 (2000).

[34] O. V. Prezhdo and Y. V. Pereverzev, J. Chem. Phys. **113**, 6557 (2000).

[35] N. Makri and W. H. Miller, J. Chem. Phys. **87**, 5781 (1987).

[36] R. Kosloff and A. D. Hammerich, Faraday Discuss. Chem. Soc. **91**, 239 (1991).

[37] S. Hammes-Schiffer and J. C. Tully, J. Chem. Phys. **101**, 4657 (1994).

[38] J. C. Burant and J. C. Tully, J. Chem. Phys. **112**, 6097 (2000).

[39] L. de Broglie, Acad. Sci. Paris **183**, 447 (1926).

[40] L. de Broglie, Acad. Sci. Paris **185**, 580 (1927).

[41] D. Bohm, Phys. Rev. **85**, 166 (1952).

[42] D. Bohm, Phys. Rev. **85**, 180 (1952).

[43] O. Maroney and B. J. Hiley, Found. Phys. **29**, 1403 (1999).

[44] B. K. Dey, A. Askar, and H. Rabitz, Chem. Phys. Lett. **297**, 247 (1998).

[45] C. L. Lopreore and R. E. Wyatt, Phys. Rev. Lett. **82**, 5190 (1999).

[46] R. E. Wyatt, J. Chem. Phys. **111**, 4406 (1999).

[47] E. Gindensperger, C. Meier, and J. A. Beswick, J. Chem. Phys. **113**, 9369 (2000).

[48] S. T. Epstein, in *Force Concept in Chemistry* (Van Nostrand Reinhold, New York, 1981), pp. 1–38.