Geometric energy transfer in two-component systems

Ryan Requist¹, Chen Li² and Eberhard K. U. Gross¹

¹Fritz Haber Center for Molecular Dynamics, Institute of Chemistry
Hebrew University of Jerusalem, Safra Campus, Jerusalem 91904, Israel
²Beijing National Laboratory for Molecular Sciences, College of
Chemistry and Molecular Engineering, Peking University, Beijing
100871, People’s Republic of China

Factoring a wave function into marginal and conditional factors partitions the subsystem kinetic energy into two terms. The first depends solely on the marginal wave function, through its gauge-covariant derivative, while the second depends on the quantum metric of the conditional wave function over the manifold of marginal variables. We derive an identity for the rate of change of the second term.

This article is part of the theme issue ‘Chemistry without the Born–Oppenheimer approximation’.

1. Introduction

Exposing a molecule to a visible or UV electromagnetic pulse excites primarily the electronic degrees of freedom. On a longer time scale, the electrons transfer energy to the nuclei. While energy transfer can be evaluated with knowledge of the electron–nuclear wave function, given a choice of nuclear subsystem, to gain deeper insight into excited state molecular dynamics, optimize control of molecular motion and bond breaking, and engineer molecular scale mechanical motion, it would be valuable to have a formula expressing the energy transfer in terms of simple fundamental quantities.

Using the exact factorization (EF) formalism [1,2], which involves the factorization of a two-component wave function into a product of marginal and conditional amplitudes [3], we have derived Ehrenfest identities [4] for the time rate of change of the kinetic energy,
momentum and angular momentum of the nuclear subsystem. By evaluating the commutators in the Heisenberg equations of motion, we found that a novel quantum mechanical force operator appeared in all three identities. In terms of this force operator, all three identities could be put in a form directly analogous to the classical equations of motion \(dE/dt = \mathbf{F} \cdot \mathbf{v},\ d\mathbf{P}/dt = \mathbf{F}\) and \(dL/dt = \mathbf{R} \times \mathbf{F} \).

One wrinkle in those results was the fact that the classical force-times-velocity form could only be achieved for the rate of change of one part of the nuclear kinetic energy, namely the term

\[
T_{n,marg} = \langle \chi(t) | \sum_{i=1}^{N_n} \frac{1}{2M_i} (\hat{P}_i + \hat{A}_i(t))^2 | \chi(t) \rangle, \tag{1.1}
\]

where \(| \chi(t) \rangle\) is the nuclear wave function that satisfies the effective Schrödinger equation

\[
i\hbar \partial_t \chi(R, t) = \sum_{i=1}^{N_n} \frac{1}{2M_i} [ -i\nabla_R + \mathbf{A}_i(R, t) ]^2 \chi(R, t) + \mathcal{E}(R, t) \chi(R, t) \tag{1.2}
\]

of the exact factorization method; \(\mathbf{R}\) denotes the set \(\{ \mathbf{R}_i \}\) of \(N_n\) nuclear coordinates. \(T_{n,marg}\) is the kinetic energy of a fictitious closed quantum system acted upon by scalar and vector potentials \(\mathcal{E}(R, t)\) and \(\mathbf{A}_i(R, t)\) (defined below). In other words, it is simply the kinetic energy one would write down if one were given the Schrödinger equation (1.2) but not told it describes only one component of a two-component system. Since \(\chi\) is the marginal probability amplitude for the nuclear component of a system of electrons and nuclei, we call \(T_{n,marg}\) the marginal nuclear kinetic energy.

The closed system described by equation (1.2) reproduces the true \(N_n\)-body density and \(N_n\)-body current density of the nuclear subsystem, but it is fictitious in the sense that off-diagonal elements of the nuclear density matrix and hence non-local observables of the nuclear subsystem cannot be calculated directly from the wave function \(\chi(R, t)\). A prime example is the true nuclear kinetic energy as obtained from the full wave function \(|\Psi(t)\rangle\) which obeys the identity [5,6]

\[
T_n = \langle \Psi(t) | \sum_{i=1}^{N_n} \frac{\hat{P}_i^2}{2M_i} | \Psi(t) \rangle = T_{n,marg} + T_{n,geo}, \tag{1.3}
\]

where the additional contribution is

\[
T_{n,geo} = \int d\mathbf{R} |\chi(R, t)\rangle^2 \sum_{i=1}^{N_n} \frac{1}{2M_i} (\langle \nabla_R, \Phi(t) | \nabla_R, \Phi(t) \rangle - | \mathbf{A}_i(R, t) |^2), \tag{1.4}
\]

with \(\mathbf{A}_i(R, t) = \text{Re} (\Phi(t) | \hat{\mathbf{P}}_i | \Phi(t))\) being the vector potential and \(| \Phi(t) \rangle\) the ket corresponding to the electronic wave function \(\Phi(r, t | \mathbf{R}) = \Psi(r, R, t) / \chi(R, t)\) conditional on \(\mathbf{R}\). The Ehrenfest identity of Li et al. [4] provides a straightforward way to calculate \(dT_{n,marg}/dt\) but gives no information about \(dT_{n,geo}/dt\).

Our main result is an exact identity for \(dT_{n,geo}/dt\), expressed in terms of primitive quantities. An interesting outcome of the derivation is the appearance of a new rank-3 quantum geometric quantity that cannot be expressed in terms of lower-rank quantities defined on \(R\)-space.

The integrand of (1.4) has geometric significance itself, as it can be expressed [7,8] in terms of a tensor contraction between \(\mathcal{I}^{\mu\nu}\), a symmetric inverse inertia tensor, and a Riemannian metric [9]

\[
g_{\mu\nu}(Q) = \text{Re} (| \mathbf{P}_\mu - A_\mu | | \mathbf{P}_\nu - A_\nu |) \tag{1.5}
\]

on nuclear configuration space, i.e. the manifold \(Q\) with generalized coordinates \(\{Q^\mu\}\) collectively denoted \(Q\). Thus, we have

\[
T_{n,geo} = \int dQ |\chi(Q)\rangle^2 \frac{1}{2} \mathcal{I}^{\mu\nu} g_{\mu\nu}(Q), \tag{1.6}
\]
which we call the geometric part of the nuclear kinetic energy. As all quantities except \( I^{\mu\nu} \) are time dependent, we suppress the time argument here and hereafter. In (1.5) and (1.6), we have switched to a tensor calculus notation, i.e. subscripts/superscripts correspond to the covariant/contravariant indices of a tensor on \( Q \), and we have generalized to a Watsonian kinetic energy operator \( \hat{T}_n = (1/2)I^{\mu\nu}P_\mu P_\nu \) [10] with \( P_\mu = -i\partial/\partial Q^\mu \) and an implicit summation convention. The metric in equation (1.5) is the EF counterpart of the quantum metric tensor originally studied in the Born–Oppenheimer (BO) approximation [11–14]. The quantum metric tensor has recently attracted attention in condensed matter physics, where its applications are too numerous to cite here.

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The usual laboratory frame kinetic energy operator, cf. equation (1.3), is a special case of the Watsonian kinetic energy, in which the set of \( Q^\mu \) is \( \{ R_{1x}, R_{1y}, R_{1z}, R_{2x}, R_{2y}, R_{2z}, \ldots \} \) and \( I^{\mu\nu} \) is diagonal and \( Q^\mu \)-independent, i.e. \( I^{\mu\nu} = I^{\alpha\beta} = M_i^{-1}\delta_{\alpha\beta} \) with \( i \) labelling the nucleus and \( \alpha = x, y, z \). The Watson form encompasses two additional cases: (1) an isolated molecule after removing the centre-of-mass coordinate [15]; and (2) a system described by a distinguished set of relevant collective coordinates. The phonon modes of a crystalline solid described with Born–von Karman boundary conditions are an example of case (2) in which \( Q^\mu \) comprise the normal mode amplitudes \( U_q \), with quasi-momentum \( q \) and branch \( \lambda \), \( I^{\mu\nu} = I^{\delta\lambda} = M_k^{-1}\delta_{q\delta}\delta_{\lambda\lambda} \) is off-diagonal and \( M_k \) is the effective mass of the normal mode [16]. In case (2), \( I^{\mu\nu} \) will be \( Q^\mu \)-dependent when \( Q \) is non-Euclidean, which can arise e.g. in an approximate reduced description in terms of a restricted set of collective coordinates. In the case of an isolated molecule in which only the centre-of-mass coordinate is removed, it is always possible to choose translationally invariant coordinates such that \( I^{\mu\nu} \) is \( Q^\mu \)-independent [8,15]; such an \( I^{\mu\nu} \) is generally non-diagonal but can be further diagonalized. Here, for simplicity, we assume \( I^{\mu\nu} \) is \( Q^\mu \)-independent but not necessarily diagonal.

2. Exact factorization formalism

To derive an identity for \( dT_{n, geo}/dt \) that does not invoke the BO approximation, we make use of the exact factorization formalism [1–3], the essential elements of which we briefly review here.

Starting from the full wave function \( \Psi(q, Q) = \langle q, Q|\psi \rangle \), where \( q \) and \( Q \) denote the sets of electronic and nuclear coordinates, one defines the nuclear wave function

\[
\chi(Q) = e^{i\mu(Q)}|\chi(Q)|, \tag{2.1}
\]

which is the marginal probability amplitude corresponding to the marginal probability

\[
|\chi(Q)|^2 = \int dq|\Psi(q, Q)|^2, \tag{2.2}
\]

and the arbitrary gauge \( \lambda(Q) \). The conditional electronic wave function

\[
\Phi(q|Q) = \frac{\Psi(q, Q)}{\chi(Q)} \tag{2.3}
\]

depends parametrically on \( Q \) and satisfies the equation

\[
i\partial_t|\Phi\rangle = (H^{BO} - \mathcal{E})|\Phi\rangle + \frac{1}{2} I^{\mu\nu}(P_\mu - A_\mu)(P_\nu - A_\nu)|\Phi\rangle + I^{\mu\nu}(P_\mu + A_\mu)\chi(P_\nu - A_\nu)|\Phi\rangle, \tag{2.4}
\]

where \( \hat{H}^{BO} = \hat{H} - \hat{T}_n \) and \( \mathcal{E} = \langle \Phi|\hat{H}^{BO}|\Phi\rangle + \mathcal{E}_{geo} - i\langle \Phi|\partial_t|\Phi\rangle \) with \( \mathcal{E}_{geo} = (1/2)I^{\mu\nu}g_{\mu\nu} \); \( \hat{H} \) is the usual non-relativistic molecular Hamiltonian in atomic units.
3. Derivation of the main result

Starting from equation (1.6), we obtain
\[
\frac{dT_{n,\text{geo}}}{dt} = \int dQ \frac{\partial |\chi(Q)|^2}{\partial t} \mathcal{E}_{\text{geo}}(Q) + \int dQ |\chi(Q)|^2 \partial_t \mathcal{E}_{\text{geo}}(Q) = \int dQ [-\partial_t J^\mu(Q)] \mathcal{E}_{\text{geo}}(Q) + \int dQ |\chi(Q)|^2 \partial_t \mathcal{E}_{\text{geo}}(Q) = \int dQ J^\mu(Q) \partial_t \mathcal{E}_{\text{geo}}(Q) + \int dQ |\chi(Q)|^2 \partial_t \mathcal{E}_{\text{geo}}(Q),
\]
(3.1)

where \(J^\mu\) is the nuclear current density
\[
J^\mu = \mathcal{I}^{\mu\nu} \text{Re} \langle \chi^*(P_\nu + A_\nu) \chi \rangle.
\]
(3.2)

In the second line of equation (3.1), we have used the continuity equation, and in the third line, we have performed integration by parts and assumed that the boundary term vanishes; this is generally true for finite systems. Focusing on \(\mathcal{E}_{\text{geo}} = (1/2) \mathcal{I}^{\mu\nu} g_{\mu\nu}\) in the second term and noting that \(\mathcal{I}^{\mu\nu}\) is time-independent, our first step is to evaluate \(\partial g_{\mu\nu} / \partial t\):
\[
\frac{\partial g_{\mu\nu}}{\partial t} = \text{Re} (P_\mu - A_\mu) \Phi |(P_\nu - A_\nu) \partial_t \Phi\rangle + \text{Re} (P_\mu - A_\mu) \partial_t \Phi |(P_\nu - A_\nu) \Phi\rangle.
\]
(3.3)

After contraction with \(\mathcal{I}^{\mu\nu}\), these two terms give equal contributions to \(\partial \mathcal{E}_{\text{geo}}\). There are no \(\partial_t A_\mu\) contributions because \(\text{Re} \langle \Phi |(P_\mu - A_\mu) \Phi\rangle = 0\). The terms on the right-hand side of equation (2.4) give the following contributions to the first term in equation (3.3):
\[
\begin{align*}
\frac{\partial g_{\mu\nu}^{(1a)}}{\partial t} &= -\text{Re} (P_\mu - A_\mu) \Phi |\partial_t \hat{H}^{\text{BO}} \Phi\rangle \\
&\quad + \text{Im} (P_\mu - A_\mu) \Phi |(\hat{H}^{\text{BO}} - \mathcal{E})(P_\nu - A_\nu) \Phi\rangle, \\
\frac{\partial g_{\mu\nu}^{(1b)}}{\partial t} &= \text{Im} (P_\mu - A_\mu) \Phi |(P_\nu - A_\nu) \frac{1}{2} \mathcal{I}^{\sigma\tau} (P_\sigma - A_\sigma)(P_\tau - A_\tau) \Phi\rangle \\
&\quad + \frac{1}{2} \mathcal{I}^{\sigma\tau} \text{Im} (P_\nu - A_\nu)(P_\mu - A_\mu) \Phi |(P_\sigma - A_\sigma)(P_\tau - A_\tau) \Phi\rangle.
\end{align*}
\]
(3.4)

The (1a) term can be put in various forms but none is simpler than the others. The second term on the right-hand side of \(\partial g_{\mu\nu}^{(1a)} / \partial t\) vanishes upon contraction with the symmetric tensor \(\mathcal{I}^{\mu\nu}\) because
\[
\mathcal{I}^{\mu\nu} (P_\mu - A_\mu) \Phi |(\hat{H}^{\text{BO}} - \mathcal{E})(P_\nu - A_\nu) \Phi\rangle
\]
(3.5)
is real. Turning to the (1b) term and moving \((P_\nu - A_\nu)\) into the bra, we obtain
\[
\frac{\partial g_{\mu\nu}^{(1b)}}{\partial t} = -\frac{1}{2} \mathcal{I}^{\sigma\tau} \partial_{\t} \text{Re} (P_\mu - A_\mu) \Phi |(P_\sigma - A_\sigma)(P_\tau - A_\tau) \Phi\rangle \\
&\quad + \frac{1}{2} \mathcal{I}^{\sigma\tau} \text{Im} (P_\nu - A_\nu)(P_\mu - A_\mu) \Phi |(P_\sigma - A_\sigma)(P_\tau - A_\tau) \Phi\rangle.
\]
(3.6)

The second term drops out upon contraction with the symmetric tensor \(\mathcal{I}^{\mu\nu}\) because
\[
\langle \mathcal{I}^{\mu\nu}(P_\nu - A_\nu)(P_\mu - A_\mu) \Phi |\mathcal{I}^{\sigma\tau} (P_\sigma - A_\sigma)(P_\tau - A_\tau) \Phi\rangle
\]
(3.7)
is real. Therefore, the contribution of the (1b) term to \(\partial \mathcal{E}_{\text{geo}} / \partial t\) is
\[
\frac{\partial \mathcal{E}_{\text{geo}}^{(1b)}}{\partial t} = -\frac{1}{4} \mathcal{I}^{\mu\nu} \partial_{\t} C_{\mu\sigma\tau} \mathcal{I}^{\sigma\tau},
\]
(3.8)
where we defined
\[
C_{\mu\nu\tau} = \text{Re} (P_\mu - A_\mu) \Phi |(P_\nu - A_\nu)(P_\tau - A_\tau) \Phi\rangle,
\]
(3.9)
a manifestly gauge invariant quantity that will be examined in §5.
For the (1c) term, we obtain
\[
\frac{\partial \sigma_{\mu \nu}^{(1c)}}{\partial t} = \text{Im} \left[ (P_\mu - A_\mu) \phi (P_\nu - A_\nu)(P_\tau - A_\tau) \phi \mathcal{I}^{\tau \sigma} \frac{(P_\sigma + A_\sigma) \chi}{\chi} \right] + \text{Im} \left[ (P_\mu - A_\mu) \phi (P_\tau - A_\tau) \phi \mathcal{I}^{\tau \sigma} P_\nu \frac{(P_\sigma + A_\sigma) \chi}{\chi} \right].
\] (3.10)

The first term simplifies to
\[
\frac{\partial \sigma_{\mu \nu}^{(1c)}}{\partial t} = -\frac{1}{2} C_{\mu \nu \tau} \mathcal{I}^{\tau \sigma} \frac{\partial_\sigma |\chi|^2}{|\chi|^2} + D_{\mu \nu \tau} \frac{f^\tau}{|\chi|^2},
\] (3.11)

where we introduced the definition
\[
D_{\mu \nu \tau} = \text{Im} \left[ (P_\mu - A_\mu) \phi (P_\nu - A_\nu)(P_\tau - A_\tau) \phi \right].
\] (3.12)

The second term of equation (3.10) gives
\[
\frac{\partial \sigma_{\mu \nu}^{(1c,ii)}}{\partial t} = -\eta_{\mu \nu} \tau \mu \tau \nu \partial_\sigma |\chi|^2 - \frac{1}{2} B_{\mu \nu \tau} \mathcal{I}^{\tau \sigma} \partial_\sigma |\chi|^2,
\] (3.13)

where \( B_{\mu \nu} = \partial_\mu A_\nu - \partial_\nu A_\mu \) is the Berry curvature. Summing equations (3.11) and (3.13) and contracting with \( \frac{1}{2} \mathcal{I}^{\mu \nu} \), we obtain
\[
\frac{\partial \epsilon_{\text{geo}}^{(1c)}}{\partial t} = -\frac{1}{4} C_{\mu \nu \tau} \mathcal{I}^{\tau \sigma} \frac{\partial_\sigma |\chi|^2}{|\chi|^2} - \frac{1}{2} \mathcal{I}^{\tau \sigma} \tau \mu \tau \nu \partial_\sigma |\chi|^2 - \frac{1}{2} \mathcal{I}^{\mu \nu} \frac{f^\tau}{|\chi|^2},
\] (3.14)

where we used equation (5.4), derived in §5, to relate \( D_{\mu \nu \tau} \) to derivatives of \( \sigma_{\mu \nu} \), and hence to \( \partial_\tau \epsilon_{\text{geo}} \), which is an electric-like force originating from \( \epsilon_{\text{geo}} \). The antisymmetry of \( B_{\mu \nu} \) makes the contribution from the second term of equation (3.13) vanish. The second term of equation (3.14) will be seen to cancel with the first term of equation (3.1).

Putting equations (3.4), (3.8) and (3.14) together, we obtain
\[
\frac{\partial \epsilon_{\text{geo}}}{\partial t} = -\mathcal{I}^{\mu \nu} \text{Re} \langle \phi | \partial_\nu \hat{H}^{\text{BO}} | (P_\mu - A_\mu) \phi \rangle - \frac{1}{2} \mathcal{I}^{\mu \nu} \partial_\nu \epsilon_{\text{geo}} - \frac{1}{2} \mathcal{I}^{\mu \nu} B_{\tau \mu} \frac{f^\tau}{|\chi|^2},
\] (3.15)

Substituting this into equation (3.1) yields the final result
\[
\frac{d T_{n, \text{geo}}}{dt} = -\left[ dQ |\chi|^2 \mathcal{I}^{\mu \nu} \text{Re} \langle \phi | \partial_\nu \hat{H}^{\text{BO}} | (P_\mu - A_\mu) \phi \rangle \right] - \left[ dQ \frac{1}{4} \mathcal{I}^{\tau \sigma} \tau \mu \tau \nu \partial_\sigma |\chi|^2 \right] - \left[ dQ |\chi|^2 \mathcal{I}^{\mu \nu} \sigma_{\mu \nu} \partial_\nu |\chi|^2 \right].
\] (3.16)

We used the identity
\[
C_{\tau \sigma \mu} = C_{\mu \sigma \tau} + \frac{1}{2} \partial_\sigma B_{\tau \mu},
\] (3.17)

to combine the second and third terms of equation (3.15), after multiplication by \( |\chi|^2 \), into the divergence of the vector field
\[
\mathcal{I}^{\mu \nu} \left( C_{\mu \sigma \tau} |\chi|^2 \right) \mathcal{I}^{\sigma \tau},
\] (3.18)

whose volume integral, converted into a surface integral via Gauss’s theorem, generally vanishes for finite systems.

4. One-dimensional example

We illustrate the identity (3.16) for an exactly solvable one-dimensional model with two electronic states. The system is driven by a time-dependent Hamiltonian. We will track the kinetic energy of
the nuclear subsystem $T_{n,marg}$ and the geometric contribution to the nuclear kinetic energy $T_{n,geo}$ as functions of time. The Schrödinger equation is

$$i\partial_t \Psi = -\frac{1}{2} \mathcal{I} \partial_x \partial_x \Psi + \left( \begin{array}{cc} h_0 + h_3 & h_1 \\ h_1 & h_0 - h_3 \end{array} \right) \Psi. \quad (4.1)$$

Our strategy is to reverse engineer the functions $h_0(x, t), h_1(x, t)$ and $h_3(x, t)$ such that the dynamics lead to a state

$$\Psi = \chi \left( e^{i(\alpha - \varphi)/2} \cos \left( \frac{\theta}{2} \right) \right),$$

(4.2)

with a Gaussian nuclear density

$$|\chi(x, t)|^2 = \frac{1}{\sqrt{\pi} \sigma(t)} \exp \left( -\frac{[x - \bar{x}(t)]^2}{\sigma^2(t)} \right), \quad (4.3)$$

which undergoes damped oscillations determined by the functions

$$\bar{x}(t) = 1 - \frac{1}{1 + \eta t} \cos t$$

and

$$\sigma(t) = \frac{1}{3\sqrt{M}} \left[ 1 + (1 + \eta t) \cos^2 t \right].$$

(4.4)

Substituting into equation (4.1), leads to the following equations:

$$\partial_t \ln |\chi| = -\frac{1}{2} \mathcal{I} (\partial_x \ln |\chi|)(\alpha_x - \cos \theta \varphi_x) - \frac{1}{4} \mathcal{I} (\alpha_x - \cos \theta \varphi_x)$$

$$- \frac{1}{2} \mathcal{I} \sin \theta \varphi_x \varphi_x,$$

$$\theta_t = -2h_1 \sin \varphi - \mathcal{I} \sin \theta (\partial_x \ln |\chi|)\varphi_x - \frac{1}{2} \mathcal{I} \sin \theta \varphi_x$$

$$- \frac{1}{2} \mathcal{I} \theta_x (\alpha_x + \cos \theta \varphi_x),$$

$$\sin \theta \varphi_t = 2(-h_1 \cos \theta \cos \varphi + h_3 \sin \theta) + \mathcal{I} (\partial_x \ln |\chi|)\theta_x$$

$$- \frac{1}{2} \mathcal{I} \sin \theta \alpha_x \varphi_x + \frac{1}{2} \mathcal{I} \theta_x$$

and

$$\omega_t - \cos \theta \omega_t = -2(h_0 + h_1 \sin \theta \cos \varphi + h_3 \cos \theta) + \mathcal{I} \varphi_x^2 \ln |\chi| + \mathcal{I} (\partial_x \ln |\chi|)^2$$

$$- \frac{1}{4} \mathcal{I} \left\{ \alpha_x^2 + \varphi_x^2 - 2 \cos \theta \alpha_x \varphi_x \right\} - \frac{1}{4} \mathcal{I} \omega_x^2,$$

(4.5)

where subscripts denote partial differentiation, e.g. $\alpha_x = \partial_x \alpha$. Choosing a gauge such that $\chi$ is real, the first equation is equivalent to the continuity equation $\partial_t |\chi|^2 = -\partial_x J$ with the nuclear current density

$$J = \mathcal{I} |\chi|^2 A \quad (4.6)$$

and vector potential

$$A = \frac{1}{2} (\alpha_x - \cos \theta \varphi_x). \quad (4.7)$$

Assuming $|\chi(x, t)|^2$ is given by equation (4.3), we can invert the continuity equation to obtain

$$A(x, t) = -\mathcal{I}^{-1} \frac{1}{|\chi(x, t)|^2} \int_x^\infty dx' \partial_t |\chi(x', t)|^2. \quad (4.8)$$
Defining \( w = \cos \theta \), we choose a state \( \Psi(x, t) \) with
\[
\begin{align*}
\varphi(x, t) &= \eta \left( 1 - \frac{3t}{1 + 3t + e^{y(1+\eta)(x-1)}} \right) \\
\rho(x, t) &= \eta \left( 1 - \frac{3t}{1 + 3t + e^{y(1+\eta)(x-1)}} \right)
\end{align*}
\] (4.9)
and
\[
\alpha(x, t) = \int dx' \left[ 2A(x', t) + w(x', t) \partial_x \varphi(x', t) \right].
\]

The Hamiltonian parameters that follow from equation (4.5) are
\[
\begin{align*}
h_0 &= -h_1 \sin \theta \cos \varphi - h_3 \cos \theta - \frac{1}{2} \alpha_t + \frac{2}{2} \cos \varphi \eta_t + \frac{1}{2} I \partial_x^2 \ln |\chi| \\
&\quad + \frac{1}{2} I (\partial_x \ln |\chi|)^2 - \frac{1}{8} I \left[ \alpha_x^2 + \varphi_x^2 - 2 \cos \theta \alpha_x \varphi_x \right] - \frac{1}{8} I \theta_x^2,
\end{align*}
\]
\[
h_1 = \frac{1}{\sin \varphi} \left[ -\frac{1}{2} \theta_t - \frac{1}{2} I \sin \theta (\partial_x \ln |\chi|) \varphi_x - \frac{1}{4} I \sin \theta \varphi_{xx} \right]
\]
\[
\text{and}
\]
\[
h_3 = \frac{1}{\sin \theta} \left[ h_1 \cos \theta \cos \varphi + \frac{1}{2} \sin \theta \varphi_t - \frac{1}{2} I (\partial_x \ln |\chi|) \theta_x \\
&\quad + \frac{1}{4} I \sin \theta \alpha_x \varphi_x - \frac{1}{4} I \theta_{xx} \right].
\]

The identity in equation (3.16), adapted to the present model, is
\[
\frac{dT_{n,\text{geo}}}{dt} = -\int dx I \text{Im} \langle \Phi | \partial_x H^{BO} | \partial_x \Phi \rangle |\chi|^2 + \int dx I A \langle \Phi | \partial_x H^{BO} | \Phi \rangle - \int dx I g \partial_x A.
\] (4.11)

In a one-dimensional problem, the metric \( g \) becomes the scalar
\[
g = \frac{1}{4} \frac{w_x^2}{1-w^2} + \frac{1}{4} (1-w^2) \varphi_x^2,
\] (4.12)
and for completeness we record
\[
C = -\frac{1}{4} \frac{1}{1-w^2} \left[ -w(1-w^2)^2 \varphi_x^2 - 3w w_x \varphi_x + (1-w^2)(w_x \varphi_x - w x \varphi_x) \right]
\]
\[
D = \frac{1}{8} \frac{1}{1-w^2} \left[ 2 w x \varphi \left( 1-w^2 \varphi_x^2 + w_x^2 \right) - (1-w^2)(4w(1-w^2)w_x \varphi_x^2 \\
&\quad - 2(1-w^2) \varphi_x \varphi_{xx} - 2w_x w_{xx} \right].
\] (4.13)

The marginal nuclear kinetic energy can be expressed entirely in terms of \( \rho = |\chi|^2 \) and \( J \) as
\[
T_{n,\text{marg}} = \int dx \rho \left[ -\frac{I}{2} \partial_x \rho \sqrt{\rho} + \frac{J^2}{2I \rho} \right].
\] (4.14)

Using the above formulae, we have numerically verified equation (4.11) for \( M = 10 \text{a.u.}, \)
\( \eta = 0.1 \text{ (a.u.)}^{-1} \) and \( \gamma = 40 \text{ (a.u.)}^{-1} \). Snapshots of the nuclear probability density \( \rho(x, t) \) and the Hamiltonian variables \( h_0(x, t), h_1(x, t) \) and \( h_3(x, t) \) are shown in figure 1 for a series of times. The rapidly spatially varying features of \( h_3(x, t) \), always pinned near \( x = 1 \), are associated with the abrupt change of the electronic state from predominantly state 1 for \( x < 1 \) to predominantly state 2 for \( x > 1 \), as can be seen in the formula for \( \rho(x, t) \) in equation (4.9).

The time dependence of \( T_{n,\text{marg}} \) and \( T_{n,\text{geo}} \) are shown in figure 2a, and the BO-like energy \( E^{BO} = \int dx |\chi|^2 (\Phi |H^{BO} | \Phi) \) is shown in figure 2b. The total energy is the sum \( T_{n,\text{marg}} + T_{n,\text{geo}} + E^{BO} \), and it is not conserved. The peaks in \( T_{n,\text{geo}} \) occur for the times \( \pi/2, 3\pi/2, 5\pi/2, \ldots \), when the nuclear wave packet passes through the location of rapid variation of the electron state near \( x = 1 \), where \( \mathcal{E}_{\text{geo}} \) is largest, therefore yielding the maximal contribution to the \( |\chi|^2 \)-weighted integral in
Figure 1. The nuclear probability density and the Hamiltonian parameters (in a.u.) are plotted for the series of times $t_n = n\pi/2$ a.u., $n = 0, \ldots, 5$, for the one-dimensional model with $M = 10$ a.u., $\eta = 0.1$ (a.u.$)^{-1}$ and $\gamma = 40$ (a.u.$)^{-1}$. (Online version in colour.)

Figure 2. (a) The marginal and geometric parts of the nuclear kinetic energy are plotted versus time for the same parameters as figure 1. (b) The BO-like contribution to the energy is plotted versus time. $T_{n,\text{geo}}$ and $E^{BO}$ are scaled for the purposes of visualization and comparison. (Online version in colour.)

equation (1.6). It can be seen that $T_{n,\text{geo}}$ is much smaller than $T_{n,\text{marg}}$. While this is typical of molecular ground states, we have found dynamical problems in which $T_{n,\text{geo}}$ is as large as $T_{n,\text{marg}}$ [17]. Quantitative results for $T_{n,\text{geo}}$ have been reported (Suppl. Mat. of Ref. [4]).

Figure 3 shows the quantity $n_1 - n_2 = |\Phi_1(x,t)|^2 - |\Phi_2(x,t)|^2$, which is the difference in population of the two electronic states. The rapid spatial variation of the electronic state at $x = 1$ makes $E_{\text{geo}}$ relatively larger at these locations. The figure shows that the characteristic distance over which the electronic state switches from state 1 to state 2 becomes smaller as time increases. Hence, $E_{\text{geo}}$ and the peaks in $T_{n,\text{geo}}$ become larger as time progresses.
Figure 3. Grey scale density plot of the difference in population $n_1 - n_2$ of the two electronic states for the same parameters as figure 1; white corresponds to $n_1 - n_2 = 1$, black to $n_1 - n_2 = -1$.

5. Rank-3 quantum geometric quantities

Here we briefly investigate some properties of the rank-3 quantities $C_{\mu\nu\tau}$ and $D_{\mu\nu\tau}$ that appeared in the last section. Beginning with $D_{\mu\nu\tau}$, we can show that

$$D_{\mu\nu\tau} = -\Re\langle \partial_\mu \Phi | \partial_\nu \partial_\tau \Phi \rangle - \frac{1}{2} B_{\mu\nu} A_{\tau} - \frac{1}{2} B_{\mu\tau} A_{\nu} + \frac{1}{2} A_{\mu} \partial_\nu A_{\tau} + A_{\mu} \partial_\nu A_{\tau}. \quad (5.1)$$

Thus, $D_{\mu\nu\tau}$ is symmetric with respect to interchange of its second two indices. To further simplify $D_{\mu\nu\tau}$, we derive the following identity:

$$\langle \partial_\mu \Phi | \partial_\nu \partial_\tau \Phi \rangle = \partial_\nu \langle \partial_\mu \Phi | \partial_\tau \Phi \rangle - \langle \partial_\mu \partial_\nu \Phi | \partial_\tau \Phi \rangle = \partial_\nu \langle \partial_\mu \Phi | \partial_\tau \Phi \rangle - \partial_\mu \langle \partial_\nu \Phi | \partial_\tau \Phi \rangle + \partial_\mu \langle \partial_\nu \Phi | \partial_\tau \Phi \rangle - \partial_\mu \langle \partial_\nu \Phi | \partial_\tau \Phi \rangle. \quad (5.2)$$

Taking the real part, we find

$$2\Re\langle \partial_\mu \Phi | \partial_\nu \partial_\tau \Phi \rangle = \partial_\tau (g_{\mu\nu} + A_\mu A_\nu) + \partial_\nu (g_{\mu\tau} + A_\mu A_\tau) - \partial_\mu (g_{\nu\tau} + A_\nu A_\tau). \quad (5.3)$$

With this identity and equation (5.1), we obtain

$$D_{\mu\nu\tau} = -\frac{1}{2} \partial_\tau g_{\mu\nu} - \frac{1}{2} \partial_\nu g_{\mu\tau} + \frac{1}{2} \partial_\mu g_{\nu\tau}. \quad (5.4)$$

Thus, $D_{\mu\nu\tau}$ has been expressed in terms of $g_{\mu\nu}$. In fact, we have

$$D_{\mu\nu\tau} = -\Gamma_{\mu\nu\tau}. \quad (5.5)$$

where $\Gamma_{\mu\nu\tau}$ is the Christoffel symbol of the first kind in classical Riemannian geometry.

Turning to $C_{\mu\nu\tau}$, we find the expression

$$C_{\mu\nu\tau} = \Im\langle \partial_\mu \Phi | \partial_\nu \partial_\tau \Phi \rangle - A_\mu g_{\nu\tau} - A_\nu g_{\mu\tau} - A_\tau g_{\mu\nu} - A_\mu A_\nu A_\tau. \quad (5.6)$$

This is also symmetric with respect to the interchange of the second two indices. However, due to the presence of the irreducible third-order quantity $\Im\langle \partial_\mu \Phi | \partial_\nu \partial_\tau \Phi \rangle$, $C_{\mu\nu\tau}$ cannot be expressed in terms of lower-order geometric quantities and their derivatives. The symbol $\Gamma_{\mu\nu\tau} + iC_{\mu\nu\tau} = (\langle \partial_\mu - iA_\mu \rangle \Phi | (\partial_\nu - iA_\nu)(\partial_\tau - iA_\tau) \Phi)$ allows one to define a connection [18].

6. Conclusion

We derived an identity for the rate that energy is transferred to $T_{n,\text{geo}}$, the geometric part of the nuclear kinetic energy. This is the part that derives from the gradient with respect to a nuclear
coordinate acting on the parametric dependence of the electronic wave function, the latter arising from the factorization of the full wave function. Our identity complements the Ehrenfest-like identity previously derived for \(dT_{n,\text{marg}}/dt\) [4], the marginal part of the nuclear kinetic energy.

Ehrenfest identities for the expectation values of position and momentum resemble Newton’s Laws. Similarly, the Ehrenfest-like identity for \(dT_{n,\text{marg}}/dt\) has a suggestive force-times-velocity form, parallelling the classical formula for the rate of work done by a force, and therefore appears to lend itself to a classical interpretation of the nuclear motion. Indeed, the terms that appear in the force operator have a close resemblance to the corresponding terms in the force that acts on nuclei when they are treated classically [19,20].

It is not yet clear if identity (3.16) for \(dT_{n,\text{geo}}/dt\) has a simple classical interpretation. We have not been able to put it in a force-times-velocity form. In the course of evaluating \(dT_{n,\text{geo}}/dt\), we derived the equation of motion for the quantum metric \(g_{\mu\nu}\). This equation involves a new object, the rank-3 geometric quantity \(C_{\mu\nu\tau}\), which appears to be a purely quantum object.

Putting together the identities for \(dT_{n,\text{marg}}/dt\) and \(dT_{n,\text{geo}}/dt\) allows us to calculate the total rate of change of the true nuclear kinetic energy. It is hoped that these identities and the insights derived from them will help scientists control energy transfer in quantum systems.

Data accessibility. This article has no additional data.

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