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MULTISCALE BORN-OPPENHEIMER THEORY OF COLLECTIVE ELECTRON-NUCLEAR DYNAMICS IN NANOSYSTEMS

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Born-Oppenheimer theory is based on the separation in timescales between the nuclear and electron dynamics implied by the electron-to-nuclear mass ratio. This makes it naturally fit into a multiscale analysis. It is shown that a fully dynamical Born-Oppenheimer theory follows from a multiscale ansatz on the wave function and a Taylor expansion in the mass ratio. Allowing for a larger spatial scale of electron motion yields an understanding of boson, fermion, and more complex excitations that involve quasi-particles with an effective mass not equal to that of the electron. The theory involves a unified asymptotic expansion in a mass and length scale ratio, and preserves all many-body effects via accounting for the full strength of the interparticle forces. A novel mean-field theory emerges based on the fact that long-scale migration allows each electron to interact with many others on the space-time scale relevant to the coarse-grained equation. Implications for computational methods and applications to quantum nanosystems such as quantum dots, nanowires, superconducting nanoparticles, and liquid He droplets are discussed.

Keywords: Multiscale analysis; Born-Oppenheimer theory; quantum nanosystems; quasi-particles.

1. Introduction

The inertia of the nuclei relative to the low mass of the electrons imparts a multiscale character to many quantum systems of current interest in condensed matter and nanoscience. This timescale separation between nuclear and electron motions is the basis of the classic Born-Oppenheimer approximation. The question arises as to whether a deductive multiscale analysis of the coupled electronic-nuclear dynamics problem can lead to new insight into these systems, above-and-beyond that provided by the classic Born-Oppenheimer approximation and its extensions.[1–4]

In this paper, we address coupled electronic-nuclear phenomena via a deductive multiscale approach. The starting point is the time-dependent Schrödinger

equation. A multiscale ansatz on the dependencies of the wavefunction on the configuration of the electron and nuclear subsystems is then made. This is followed by a perturbation analysis in various dimensionless ratios to arrive at a coarse-grained wave equation for long-scale electron dynamics coupled to slow short-scale nuclear motions. Similar deductive mulsticale approaches have been successful in the theory of bionanosystems evolving via Newtonian all-atom dynamics[5–10] and, to a more limited extent, to quantum nanosystems.[11–14]

Deumens and Örhn[15] discussed a variety of approximations to the electron nuclear problem wherein the nuclei are treated either classically or quantum mechanically. Their END approach is developed for various approximations to the electronic wave function based on the use of orbitals centered either on the average nuclear positions or on an independent center. These END treatments do not fold the multiple time and space scale character of the wave function directly into the analysis. Also, the approximations they propose do not arise out of an asymptotic expansion starting from the full Hamiltonian. Rather, they arise out of a conjecture based on various approximations familiar in quantum chemistry for some molecular problems. In contrast, in the present theory, we integrate notions of multiple time scale analysis, balancing of spatial, temporal, and interaction strength scaling, and tie them together with a unified asymptotic expansion.

Cukier and Deutch[16] developed a multiple time scale perturbation theory to obtain the equation of motion for the spin-density matrix. This method, originating with Krylov and Bogoliubov[17] in nonlinear mechanics, has the advantage of removing secular behavior, a problem from which other time-dependent perturbation techniques suffer. Other applications in quantum mechanics include the work of Montgomery and Ruijgrok[18] on particles with spin subjected to time-dependent magnetic fields and that of Brooks and Scarfone[19] on radiative decay processes.

A novel element of the present study is that we pursue a class of phenomena wherein the long-scale electron dynamics is on a timescale comparable to slow, short scale nuclear motion. As with the work of Cukier and Deutch,[16] we make the ansatz that the function of interest (here the wave function and later the density matrix) depends on time in multiple ways. The latter is introduced in terms of a sequence of time variables $t_n = \varepsilon^n t$ where the smallness parameter ε arises as a measure of the strength of various interaction terms in the Hamiltonian. However, in the present treatment, we start with the Schrödinger equation, rather than the Liouville equation, and we balance the interaction terms in the Hamiltonian with new ones arising from the multiple spatial and mass scales for the electronic and nuclear configuration. In particular, we investigate a united limit wherein the electron-nuclear mass ratio and the average nearest-neighbor electron distance to the characteristic length of electron motion are tied to the unifying smallness parameter ε. This enables a powerful unified perturbation scheme in ε. The implication of the analysis is that nuclear motion can be coupled over long distances via low-lying, long spatial scale disturbances of electron density. In this way, a coarse-grained wave equation (CGWE) for coupled nuclear-electronic dynamics

is obtained. The coarse-grained wave function we obtain depends on long spatial scale electronic configuration variables and short-scale nuclear ones, an interesting feature whereby two subsystems are coupled directly on distinct scales in one CGWE. In addition, we demonstrate the equivalence of the long-time and ground state expectation values which plays a key role in removing secular terms to arrive at the CGWE. A scaling ansatz on the wave function is introduced (Sec. 2) and a multiscale perturbation scheme is developed (Sec. 3). The CGWE is analyzed via a novel coarse-grained mean-field (CGMF) approximation that is distinct from the Hartree-Fock approximation (Sec. 4). Conclusions, implications for computational algorithms, and potential applications to quantum nanosystems are discussed (Sec. 5).

2. Scaling the Electron Problem

A many-particle system may involve disturbances on a variety of length scales. To address this, a formalism can be developed wherein the wave function is taken to depend on a variety of configuration variables. Let $\Gamma = \{\vec{r}_1, \ldots, \vec{r}_N\}$ specify the N-particle configuration and ε be the ratio of the smallest characteristic length to that of the next highest one. Then, the sequence of configuration variables $\Gamma_{(n)}$ (for $n = 0, 1, \ldots$) can be introduced such that

$$\Gamma_{(n)} = \varepsilon^n \Gamma. \tag{2.1}$$

With this, the ansatz is made such that

$$\Upsilon(\Gamma, t) = \Psi(\Gamma_{(0)}, \Gamma_{(1)}, \ldots; t_0, \underline{t}; \varepsilon) \tag{2.2}$$

for $t_n = \varepsilon^n t$ and $t = \{t_1, t_2, \ldots\}$. Putting the ansatz of Eq. (2.1) into the wave equation and using the chain rule, one obtains

$$i\hbar \sum_{n=0}^{\infty} \varepsilon^n \frac{\partial \Psi}{\partial t_n} = (H_0 + \varepsilon H_1 + \cdots)\Psi\,. \tag{2.3}$$

We divide the N-particle potential such that

$$V = \sum_{n=0}^{\infty} \varepsilon^{2n} V_n(\Gamma_{(0)}, \ldots, \Gamma_{(n)})\,, \tag{2.4}$$

and show that this framework yields a self-consistent approach as follows. Note that V_n only depends on the shorter scales (i.e. $\Gamma_{(0)}, \ldots, \Gamma_{(n)}$) and not the longer ones (i.e. $\Gamma_{(n+1)}, \Gamma_{(n+2)}, \ldots$) where $\underline{\nabla}$, is the $3N_e$-dimensional gradient with respect to $\Gamma_{(j)}$. With this,

$$H_n = \begin{cases} -\dfrac{\hbar^2}{m} \displaystyle\sum_{j=0}^{(n-2)/2} \underline{\nabla}_j \cdot \underline{\nabla}_{n-j} - \dfrac{\hbar^2}{2m} \nabla^2_{n/2} + V_{n/2} & \text{for } n \text{ even}, \\ -\dfrac{\hbar^2}{m} \displaystyle\sum_{j=0}^{(n-1)/2} \underline{\nabla}_j \cdot \underline{\nabla}_{n-j} & \text{for } n \text{ odd}, \end{cases} \tag{2.5}$$

3. Multiscale Born-Oppenheimer Approach

The small mass of the electron relative to that of the nuclei introduces a separation in the spatial scales over which the wave function varies. The objective of the present development is to reconstruct these dependencies. Let $\underline{r} = \{\vec{r}_1 \cdots \vec{r}_{Ne}\}$ be the set of $3N_e$ electron positions and $\underline{R} = \{\vec{R}_1 \cdots \vec{R}_{Nn}\}$ be that of the N_n nuclear (or ion core) positions. Let ε^2 be the ratio of the mass of an electron m to that of a typical nucleus M (for simplicity of presentation, we will, henceforth, assume all nuclei have the same mass M). Since the electrons are much lighter than the nuclei, it implies that they have a greater range of motion than the latter. To capture this longer-scale dependence of the wave function $\Upsilon(\underline{r}, \underline{R}, t)$ on $\underline{r}$, we introduce the scaled electron configuration $\underline{\sigma} = \varepsilon \underline{r}$.

With this, the wave function has the multiscale dependence

$$\Upsilon(\underline{r}, \underline{R}, t) = \Psi(\underline{r}, \underline{\sigma}(\underline{r}), \underline{R}; t_0(t), \underline{t}(t); \varepsilon), \tag{3.1}$$

where $\underline{t} = \{t_1, t_2, \ldots\}$ for scaled time $t_n = \varepsilon^n t \quad (n = 0, 1, \ldots)$. The above ansatz captures the dynamic coupling of short electron and nuclear motion (via $\underline{r}$ and $\underline{R}$) with longer scale dynamics expressed via the σ dependence. As the wave function has multiple dependences on the electron configuration, it also must have corresponding dependencies on time, hence the introduction of the set of scaled times $\{t_0, \underline{t}\}$. This framework is similar to that used for other quantum[11–14] and classical[5–10] many-particle problems. The overall objective is to solve the wave equation as an asymptotic expansion in ε and arrive at a coarse-grained wave equation for the longer electron ($\underline{\sigma}$) and shorter nuclear ($\underline{R}$) behavior of the system.

Placing the ansatz of Eq. (3.1) in the wave equation for the coupled electron-nuclear system and using the chain rule, one obtains

$$i\hbar \sum_{n=0}^{\infty} \varepsilon^n \frac{\partial \Psi}{\partial t_n} = \left(H_0 + \varepsilon H_1 + \varepsilon^2 H_2\right) \Psi, \tag{3.2}$$

$$H_0 = -\frac{\hbar^2}{2m} \nabla_{\underline{r}}^2 + V_0(\underline{r}, \underline{R}), \tag{3.3}$$

$$H_1 = -\frac{\hbar^2}{m} \underline{\nabla}_{\underline{r}} \cdot \underline{\nabla}_{\underline{\sigma}}, \tag{3.4}$$

$$H_2 = -\frac{\hbar^2}{2m} \nabla_{\underline{\sigma}}^2 - \frac{\hbar^2}{2m} \nabla_{\underline{R}}^2 + V_1(\underline{r}, \underline{\sigma}, \underline{R}), \tag{3.5}$$

where $\underline{\nabla}_{\underline{r}}, \underline{\nabla}_{\underline{\sigma}}$, and $\underline{\nabla}_{\underline{R}}$ are the $\underline{r}$, $\underline{\sigma}$, and $\underline{R}$ gradients respectively.

This framework makes ε the dependencies of Ψ on configuration, time, and ε explicit. The latter facilitates the solution of the problem in the perturbed form $\Psi = \sum_{n=0}^{\infty} \varepsilon^n \Psi_n$. With this, the coefficient functions are determined by replacing Ψ in Eq. (3.2) as a perturbation expansion and comparing terms order by order.

To $O(\varepsilon^0)$, the unfolded wave equation (Eq. (3.2)) takes the form

$$i\hbar\frac{\partial\Psi_0}{\partial t_0} = H_0\Psi_0\,. \tag{3.6}$$

We focus on the family of solutions generated by the ground state $\hat{\Psi}$ of H_0. We adopt the convention that $\hat{\Psi}$ has energy zero (i.e. $H_0\hat{\Psi} = 0$). With this, Eq. (3.6) admits a solution in the form

$$\Psi_0 = \hat{\Psi}(\underline{r}, \underline{R})W(\underline{\sigma}, \underline{R}, \underline{t}), \tag{3.7}$$

where the factor W is found to satisfy a coarse-grained wave equation when the treatment is carried out to $O(\varepsilon^2)$ as follows.

To $O(\varepsilon)$, we obtain

$$i\hbar\left(\frac{\partial\Psi_1}{\partial t_0} + \frac{\partial\Psi_0}{\partial t_1}\right) = H_0\Psi_1 + H_1\Psi_0\,. \tag{3.8}$$

Inserting Eqs. (3.3) and (3.7), Eq. (3.8) admits the solution

$$\Psi_1 = -t_0|0\rangle\frac{\partial W}{\partial t_1} - \frac{i}{\hbar}\int_{-t_0}^{0} dt_0^{'}S(-t_0^{'})H_1(W|0\rangle), \tag{3.9}$$

where $S(t_0)$ denotes the evolution operator $\exp(-i(H_0 - i0^+)t_0/\hbar)$, the bra-ket notation $|0\rangle$ is used to represent $\hat{\Psi}$, and the initial value of Ψ_1 is taken to be zero. The positive infinitesimal 0^+ is introduced to ensure the evolution operator vanishes when $t_0 \to \infty$.

As earlier,[13,14] we introduce a theorem analogous to the Gibbs hypothesis from classical statistical mechanics. Here, this theorem states that the long-time average and expectation value are equal:

$$\lim_{t_0\to\infty}\tfrac{1}{t_0}\int_{-t_0}^{0} dt_0^{'}S(-t_0^{'})\Omega|0\rangle = |0\rangle\langle 0|\Omega|0\rangle, \tag{3.10}$$

$$\langle 0|\Omega|0\rangle \equiv \int d^{3N_e}\underline{r}\hat{\Psi}^*\Omega\hat{\Psi}, \tag{3.11}$$

for any time-independent operator Ω.

Examination of Eq. (3.9) shows that for Ψ_1 to be well-behaved, the t_0 divergent terms must be counterbalanced as $t_0 \to \infty$ or if there are no such counterbalancing terms, then W must be independent of t_1. Multiplying both sides by $1/t_0$ and letting $t_0 \to \infty$, we obtain

$$|0\rangle\frac{\partial W}{\partial t_1} = \frac{i\hbar}{m}|0\rangle\sum_{q=1}^{N_e}\langle 0|\frac{\partial}{\partial\vec{r}_q}|0\rangle\cdot\frac{\partial W}{\partial\vec{\sigma}_q}. \tag{3.12}$$

Since $H_0|0\rangle = 0$ and thus so is $\langle 0|H_0$, the uniqueness of $\hat{\Psi}$ for the non-degenerate case implies $\hat{\Psi}$ can be taken as real without loss of generality. With

this, $\langle 0|\partial/\partial\vec{r}_q|0\rangle = \frac{1}{2}\int d\underline{r}\partial\hat{\Psi}^2/\partial\vec{r}_q$. Since $\hat{\Psi}$ vanishes at the boundaries, we find that $\langle 0|\partial/\partial\vec{r}_q|0\rangle = 0$. With this, we obtain

$$\frac{\partial W}{\partial t_1} = 0\,, \tag{3.13}$$

and Ψ_1 takes the form

$$\Psi_1 = -\frac{i}{\hbar}\int_{-t_0}^{0} dt_0^{'} S(-t_0^{'}) H_1(W|0\rangle). \tag{3.14}$$

To $O(\varepsilon^2)$, the wave equation (Eq. (3.2)) implies

$$i\hbar\left(\frac{\partial\Psi_2}{\partial t_0} + \frac{\partial\Psi_1}{\partial t_1} + \frac{\partial\Psi_0}{\partial t_2}\right) = H_0\Psi_2 + H_1\Psi_1 + H_2\Psi_0\,. \tag{3.15}$$

This admits the solution

$$\Psi_2 = -\int_{-t_0}^{0} dt_0^{'} S(-t_0^{'})\left\{\frac{\partial\Psi_0}{\partial t_2} + \frac{\partial\Psi_1}{\partial t_1} + \frac{i}{\hbar}H_1\Psi_1 + \frac{i}{\hbar}H_2\Psi_0\right\}, \tag{3.16}$$

where the value of Ψ_2 at $t_0 = 0$ is taken to be zero. Inserting Eqs. (3.3)–(3.5), (3.7), and (3.14) in Eq. (3.16) and examining the long time behavior, we find that the condition guaranteeing Ψ_2 is well-behaved as $t_0 \to \infty$ yields

$$i\hbar\frac{\partial W}{\partial t_2} = H^{CG}W, \tag{3.17}$$

$$H^{CG} = V^{CG}(\underline{\sigma}, \underline{R}) - \frac{\hbar^2}{2m}\nabla^2_{\underline{R}} + \sum_{q,q'=1}^{N_e}\sum_{\alpha,\alpha'=1}^{3}\mu_{q\alpha q'\alpha'}\frac{\partial^2}{\partial\sigma_{q\alpha}\partial\sigma_{q'\alpha'}}, \tag{3.18}$$

$$V^{CG} = \langle 0|V_1|0\rangle - \frac{\hbar^2}{2m}\langle 0|\nabla^2_{\underline{R}}|0\rangle, \tag{3.19}$$

$$\mu_{q\alpha q'\alpha'} = -\frac{\hbar^2}{2m}\delta_{qq'}\delta_{\alpha\alpha'} + \frac{i\hbar}{m^2}\int_{-\infty}^{0} dt_0\chi_{q\alpha q'\alpha'}(t_0), \tag{3.20}$$

$$\chi_{q\alpha q'\alpha'}(t_0) = \langle 0|p_{q\alpha}S(-t_0)p_{q'\alpha'}|0\rangle, \tag{3.21}$$

where $\vec{p}_q$ is the momentum of electron q (i.e. $\vec{p}_q = -i\hbar\partial/\partial\vec{r}_q$).

By using the completeness of the eigenfunctions $|n\rangle$ of H_0 and the fact that $\langle 0|p_{q\alpha}|0\rangle = 0$ for the nondegenerate case, one can show[14] that if $|n\rangle$ is fermionic and independent of the long electron motion (i.e. of σ), then the matrix μ is independent of the particle label and Eq. (3.20) is reduced to

$$\mu_{\alpha\alpha'} = -\frac{\hbar^2}{2m}\delta_{\alpha\alpha'} + \tilde{\chi}_{\alpha\alpha'}, \tag{3.22}$$

$$\tilde{\chi}_{\alpha\alpha'} = -\frac{\hbar^2}{m^2}\sum_{n\neq 0}\frac{\langle 0|p_\alpha|n\rangle\langle n|p_{\alpha'}|0\rangle}{\varsigma_n}, \tag{3.23}$$

where p_α is the α component of the momentum of any single electron, $H_0|n\rangle = \varsigma_n|n\rangle$, $\varsigma_n > 0$ for $n > 0$, and $\varsigma_0 = 0$.

4. Coarse-grained Mean-field Theory of Plasmon-Nuclear Motion Interactions

The formulation of the previous section describes the interaction of slow nuclear motion with long wavelength electron density excitations. Through such an interaction, nuclei moving in one region of the system can cause disturbances in the electron density which would perturb distant nuclei. To investigate this phenomenon, and other implications of the above formalism, consider a coarse-grained mean field (CGMF) approximation as follows.

As suggested earlier,[14] on the long space-time scales for which the CGWE of Sec. 3 operates, each electron interacts with many others. In this case, one expects that, to good approximation, the electrons experience mean-field dynamics. With this, we explore solutions to the CGWE (Eq. (3.17)) that are stationary and of the variational form

$$W(\underline{\sigma},\underline{R}) = \Phi(\underline{R})Z(\underline{\sigma}), \tag{4.1}$$

$$Z(\underline{\sigma}) = \prod_{\ell=1}^{N_e} \psi(\vec{\sigma}_\ell). \tag{4.2}$$

Equations for Φ and ψ can be obtained by minimizing the variational energy E^{CG} defined by

$$E^{CG} = \frac{\langle W|H^{CG}|W\rangle}{\langle W|W\rangle}, \tag{4.3}$$

where the inner products involve integration over all $\underline{\sigma}$, $\underline{R}$ space. With the above mean-field form for W, the equations implied by $\delta E^{CG}/\delta\Phi = 0$ and $\delta E^{CG}/\delta\psi = 0$ become

$$\left\{F[\underline{R};\psi] - \frac{\hbar^2}{2m}\nabla^2_{\underline{R}}\right\}\Phi(\underline{R}) = E^{CG}\Phi(\underline{R}), \tag{4.4}$$

$$\left\{Q[\vec{\sigma};\Phi] + \sum_{\alpha,\alpha'=1}^{3}\beta_{\alpha\alpha'}\frac{\partial^2}{\partial\sigma_\alpha\partial\sigma_{\alpha'}}\right\}\psi(\vec{\sigma}) = \tilde{E}^{CG}\psi(\vec{\sigma}), \tag{4.5}$$

where

$$\begin{aligned} F[\underline{R};\psi] = &\int d^{3N_e}\underline{\sigma}\mathrm{Z}(\underline{\sigma})V^{CG}(\underline{\sigma},\underline{R})\mathrm{Z}(\underline{\sigma}) \\ &+ N_e\sum_{\alpha,\alpha'=1}^{3}\mu_{\alpha\alpha'}(\underline{R})\int d^3\sigma\psi(\vec{\sigma})\frac{\partial^2\psi(\vec{\sigma})}{\partial\sigma_\alpha\partial\sigma_{\alpha'}} \\ &+ N_e(N_e-1)\sum_{\alpha,\alpha'=1}^{3}\mu_{\alpha\alpha'}(\underline{R})\int d^3\sigma d^3\sigma'\psi(\vec{\sigma})\psi(\vec{\sigma}')\frac{\partial\psi(\vec{\sigma})}{\partial\sigma_\alpha}\frac{\partial\psi(\vec{\sigma}')}{\partial\sigma'_{\alpha'}}, \end{aligned} \tag{4.6}$$

$$Q[\vec{\sigma};\Phi] = \int d^{3N_n}\underline{R}d^3\sigma^{(1)}\cdots d^3\sigma^{(N_e-1)}\Phi^2(\underline{R})\psi^2(\vec{\sigma}^{(1)})\cdots\psi^2(\vec{\sigma}^{(N_e-1)})V^{CG}(\underline{\sigma},\underline{R}), \tag{4.7}$$

$$\beta_{\alpha\alpha'}[\Phi] = \int d^{3N_n} R\Phi^2(R)\mu_{\alpha\alpha'}(R), \tag{4.8}$$

$$\begin{aligned}\tilde{E}^{CG} = E^{CG} &+ \frac{\hbar^2}{2m}\int d^{3N_n}\underline{R}\Phi(R)\nabla^2_{\underline{R}}\Phi(\underline{R}) \\ &- (N_e-1)\sum_{\alpha,\alpha'=1}^{3}\beta_{\alpha\alpha'}\int d^3\sigma\psi(\vec{\sigma})\frac{\partial^2\psi(\vec{\sigma})}{\partial\sigma_\alpha\partial\sigma_{\alpha'}} \\ &- (N_e-1)(N_e-2)\sum_{\alpha,\alpha'=1}^{3}\beta_{\alpha\alpha'}\int d^3\sigma d^3\sigma'\psi(\vec{\sigma})\psi(\vec{\sigma}')\frac{\partial\psi(\vec{\sigma})}{\partial\sigma_\alpha}\frac{\partial\psi(\vec{\sigma}')}{\partial\sigma'_{\alpha'}}.\end{aligned} \tag{4.9}$$

This nonlinear eigenvalue problem (Eqs. (4.4) and (4.5)) yields Φ, ψ, and E^{CG}. The quantum dynamics of the nuclei described via Φ interacts with the electron density field as described by ψ to yield the coupled nuclear-plasmon disturbances.

From our earlier study, there can be more complex solutions.[14] In the above, we have assumed $\hat{\Psi}$ is antisymmetric with respect to electron exchange and is a ground state of H_0. However, overall antisymmetry can also be realized via solutions of the form

$$\Psi_0 = \Xi\hat{\Psi}W\,, \tag{4.10}$$

where Ξ antisymmetrizes functions of the N_e electron degrees of freedom. Since a ground state $\hat{\Psi}$ that is not antisymmetric has lower energy than an antisymmetric one, the total energy, i.e. due to E^{CG} plus the energy associated with $\hat{\Psi}$, can be lower than the similar quantity for antisymmetric $\hat{\Psi}$. This would imply a type of structural quantum phase transition that follows when the nuclei interact with, and via, the long-range electron dynamics.

5. Conclusions and Prospective

The deductive multiscale analysis of Secs. 2 and 3 yields a new perspective on coupled nuclear-electronic dynamics. It corresponds to the quantum dynamics of slow nuclear motions with long-scale electronic excitations as manifest in the coarse-grained wave function W and accompanying wave equation. When the base state $\hat{\Psi}$ of the lowest order electronic problem (at frozen nuclei) is antisymmetric, W must be symmetric with respect to electron exchange, suggesting that the long-range electron motion is bosonic in character, and thus corresponds, for example, to plasmon excitations. As W is a coarse-grained wave function describing long-scale electronic dynamics (i.e. $\underline{\sigma}$ versus $\underline{r}$), on the space-time scale of W dynamics each electron interacts with many others, and with many nuclei. Thus, the electronic dependence of W should have mean-field character (Sec. 4). This implies the approximation wherein plasmon wave functions ψ interact with the nuclear wave function Φ, a picture leading to the coupled equations for Φ and ψ (Sec. 4). This stationary state picture can be generalized to a time-dependent one using least-action principle methods.[20] In this dynamical framework, one could explore the

semi-classical limit of nuclear motion to arrive at a novel picture of nuclear motion coupled to quantized plasmon dynamics. The coarse-grained mean-field and classical nuclear approximations suggested above hold promise for efficient simulation of quantum nanosystems like graphene, quantum dots, molecular wires, and superconducting nanoparticles. One approach is suggested by the CGMF method of Sec. 4. In our coarse-grained wave equations, the electron dynamics is mediated by effective masses and coarse-grained interactions. Earlier results[13,14] show that the coarse-grained wave equation for W is just one of several limit laws that arise for different systems, i.e. pseudo-relativistic[13] versus dressed Schrödinger[14] types (the latter having been investigated here).

Systems that have not been considered here are ones wherein the nuclei exhibit long-time behavior too. Such behavior can be accounted for by introducing scaled nucleus configuration $\Sigma = \varepsilon R$. In this formulation, the ansatz of Eq. (3.1) is rewritten as

$$\Upsilon(\underline{r}, \underline{R}, \underline{t}) = \Psi(r, \sigma(\underline{r}), \underline{R}, \underline{\Sigma}(\underline{R}); t_0(t), \underline{t}(t); \varepsilon) \tag{5.1}$$

while the solution to the $O(\varepsilon^0)$ wave equation takes the form

$$\Psi_0 = \hat{\Psi}(\underline{r}, \underline{R}) W(\underline{\sigma}, \underline{R}, \underline{\Sigma}, \underline{t})\,. \tag{5.2}$$

While the electron-electron potential V_{ee} is split as in Eq. (2.4), the electron-nucleus potential V_{en} takes the form

$$V_{en} = \sum_{\ell=1}^{N_n} \sum_{q=1}^{N_e} \left\{ \frac{\exp\left(-k|\vec{r}_q - \vec{R}_\ell|^2\right)}{|\vec{r}_q - \vec{R}_\ell|} + \varepsilon \frac{1 - \exp\left(-k|\vec{r}_q - \vec{R}_\ell|^2\right)}{|\vec{\sigma}_q - \vec{\Sigma}_\ell|} \right\}. \tag{5.3}$$

The long-range nuclear coordinates $(\vec{\Sigma}_\ell)$ can be considered frozen in many problems (e.g. solids, nanoparticles, graphene, or shorter timescale phenomena). However, for a system like ^{3}He or ^{4}He, the $\underline{\Sigma}$ motions must be accounted for and the theory must be carried out to $O(\varepsilon^4)$.

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