Stochastic perturbation theory: A prequel to the reptation quantum Monte Carlo method

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I present a different approach to Rayleigh-Schrödinger perturbation theory, based on Laplace transforms and polynomial theory, yielding an iterative expression for the perturbative expansion of the energy of the nondegenerate ground state of a quantum system, which easily lends itself to symbolic computation. A stochastic interpretation of the various perturbative corrections naturally leads to a resummation scheme that is equivalent to the reptation quantum Monte Carlo method and that actually provided the original motivation to its development in the late 1990s.

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I. INTRODUCTION

Perturbation theory (PT) [1] is as old as modern quantum mechanics (QM) itself [2], and is in fact one of the pillars of any elementary or advanced course in QM. PT is instrumental to most applications of QM, other than a few exactly solvable models, and has provided the ground for advanced methods, such as quantum field theory in particle and condensed-matter physics, or quantum chemistry. In spite of its ubiquity, the use of PT is restricted to low orders, as its complexity increases very steeply with the order of the theory. Nonperturbative methods, such as those based on stochastic approaches, have therefore gained popularity due to their broader applicability.

The purpose of this paper is twofold. On the one hand, it presents an alternative approach to PT, based on Laplace transforms and polynomial theory, that allows perturbative corrections to the ground-state (GS) energy of a quantum system to be derived to any order, without ever computing any corrections to the wave function. While this approach hardly broadens the scope of PT, it does provide a systematic and mathematically elegant approach to it, which easily lends itself to automatic algebraic manipulation. On the other hand, a well-established mapping between the imaginary-time evolution of a quantum system and the diffusive process of an auxiliary classical system [3] allows one to interpret the perturbative corrections as cumulants of a suitably defined random walk and suggests a resummation scheme, which is equivalent to the reptation quantum Monte Carlo (RQMC) [4,5] method and that actually provided the original motivation to its development in the late 1990s.

This paper is organized as follows: Section II presents an alternative approach to Rayleigh-Schrödinger PT, not requiring the calculation of any corrections to the wave function; Sec. III introduces the quantum-classical mapping that is propedeutic to stochastic perturbation theory and RQMC; Secs. IV and V present a stochastic interpretation of PT theory and RQMC as an effective technique to resum all the perturbative corrections up to infinite order; finally, Sec. VI contains my conclusions.

II. A DIFFERENT PATH TO RAYLEIGH-SCHRÖDINGER PERTURBATION THEORY

We want to compute the GS energy E_0 of a quantum system whose Hamiltonian $\widehat{H}$ can be split into an unperturbed term $\widehat{\mathcal{H}}$ whose spectrum is known,

$$\widehat{\mathcal{H}}\Phi_n = \mathcal{E}_n\Phi_n, \tag{1}$$

and a perturbation $\widehat{\mathcal{W}}$,

$$\widehat{H} = \widehat{\mathcal{H}} + \widehat{\mathcal{W}}. \tag{2}$$

The purpose of perturbation theory is to express E_0 as a power series in the strength of the perturbation $\mathcal{W}$. In order to streamline some of the notation, I will assume that the energy zero is chosen to coincide with the unperturbed ground state: $\mathcal{E}_0 = 0$. If the latter is not orthogonal to the exact one, one has

$$\begin{aligned} E_0 &\sim -\frac{d}{d\tau}\ln\mathcal{Z}(\tau), \\ \mathcal{Z}(\tau) &= \langle\Phi_0|e^{-\widehat{H}\tau}|\Phi_0\rangle = \sum_{n=0}^{\infty}|\langle\Phi_0|\Psi_n\rangle|^2 e^{-E_n\tau}, \end{aligned} \tag{3}$$

where E_n and Ψ_n are exact eigenpairs, $\widehat{H}\Phi_n = E_n\Phi_n$,

$$\begin{aligned} e^{-\widehat{H}\tau} = e^{-\widehat{\mathcal{H}}\tau}\Bigg(1 - \int_0^\tau d\tau_1\widehat{\mathcal{W}}(\tau_1) + \int_0^\tau d\tau_2\int_0^{\tau_2} d\tau_1\widehat{\mathcal{W}}(\tau_2)\widehat{\mathcal{W}}(\tau_1) \\ + \cdots(-)^n\int_0^\tau d\tau_n\int_0^{\tau_n} d\tau_{n-1}\cdots\int_0^{\tau_2} d\tau_1\widehat{\mathcal{W}}(\tau_n)\widehat{\mathcal{W}}(\tau_{n-1})\cdots\widehat{\mathcal{W}}(\tau_1) + \cdots\Bigg), \end{aligned} \tag{4}$$

the corresponding imaginary-time propagator, $\widehat{\mathcal{W}}(t) = e^{\widehat{\mathcal{H}}_0 \tau} \widehat{\mathcal{W}} e^{-\widehat{\mathcal{H}}_0 \tau}$ is the perturbation in the interaction representation, the "$\sim$" symbol indicates the large (imaginary-) time limit, and natural units ($\hbar = 1$) are used throughout this paper. We can thus write a perturbative expansion for $\mathcal{Z}(\tau)$ as

$$\mathcal{Z}(\tau) = 1 - \lambda_1(\tau) + \lambda_2(\tau) + \cdots (-)^n \lambda_n(\tau) + \cdots , \tag{5}$$

where

$$\lambda_n(\tau) = \int_0^\tau d\tau_n \int_0^{\tau_n} d\tau_{n-1} \cdots \int_0^{\tau_2} d\tau_1 \langle \Phi_0 | \widehat{\mathcal{W}}(\tau_n) \widehat{\mathcal{W}}(\tau_{n-1}) \cdots \widehat{\mathcal{W}}(\tau_1) | \Phi_0 \rangle \tag{6}$$

$$= \sum_{k_1 \cdots k_{n-1}} \mathcal{W}_{0k_{n-1}} \mathcal{W}_{k_{n-1}k_{n-2}} \cdots \mathcal{W}_{k_1 0} \int_0^\tau d\tau_n \int_0^{\tau_n} d\tau_{n-1} e^{-\mathcal{E}_{k_{n-1}}(\tau_n - \tau_{n-1})} \cdots \int_0^{\tau_2} d\tau_1 e^{-\mathcal{E}_{k_1}(\tau_2 - \tau_1)}, \tag{7}$$

and $\mathcal{W}_{kl} = \langle \Phi_k | \widehat{\mathcal{W}} | \Phi_l \rangle$. Note that the large-time behavior of $\lambda_n(\tau)$ is polynomial, of order n: $\lambda_n(\tau) \sim O(\tau^n)$. In order to express $\ln \mathcal{Z}$ as a power series in the strength of the perturbation $\mathcal{W}$, we define the formal moments as $\mu_n = n! \lambda_n$. The logarithm of $\mathcal{Z}$ can then be expressed as a power series in $\mathcal{W}$ as

$$-\ln \mathcal{Z}(\tau) = \kappa_1(\tau) - \frac{1}{2}\kappa_2(\tau) \cdots + \frac{(-)^{n+1}}{n!}\kappa_n(\tau) \cdots , \tag{8}$$

where the formal cumulants κ_n are defined as [6]

$$\begin{aligned} \kappa_1 &= \mu_1, \\ \kappa_2 &= \mu_2 - \mu_1^2, \\ \kappa_3 &= \mu_3 - 3\mu_2\mu_1 + 2\mu_1^3 \\ &\cdots \\ \kappa_n &= \mu_n - \sum_{k=1}^{n-1} \binom{n-1}{k} \kappa_{n-k}\mu_k. \end{aligned} \tag{9}$$

The recursive relation between moments and cumulants [Eq. (9)] is best expressed in terms of reduced cumulants $\gamma_n = \kappa_n / n!$ as

$$\gamma_n(\tau) = \lambda_n(\tau) - \sum_{k=1}^{n-1} \frac{n-k}{n} \gamma_{n-k}(\tau) \lambda_k(\tau). \tag{10}$$

We thus have

$$\begin{aligned} E_0 &= \varepsilon_1 + \varepsilon_2 + \cdots \varepsilon_n + \cdots , \\ \varepsilon_n &\sim (-)^{n+1} \dot{\gamma}_n(\tau), \end{aligned} \tag{11}$$

where ε_n is the nth-order correction and the dot indicates a derivative with respect to imaginary time.

In order for the limit implicit in Eq. (11) to exist, it is necessary that the κ's grow at most linearly with τ as $\tau \to \infty$. In many-body perturbation theory, this property is a consequence of the linked-cluster theorem [7]. I do not know how this can be demonstrated in general, other than from the tautology that the limit *must* exist. In Sec. IV, where perturbation theory will be expressed in terms of an auxiliary stochastic process, eventually leading to RQMC, this property will be shown to derive from the additivity of the cumulants of sums of independent stochastic variables.

Using Eq. (10), a recursion relation can be written for the $\dot{\gamma}$'s in terms of the λ's and their derivatives:

$$\dot{\gamma}_n(\tau) = \dot{\lambda}_n(\tau) - \sum_{k=1}^{n-1} \frac{n-k}{n} \left[\dot{\gamma}_{n-k}(\tau) \lambda_k(\tau) + \gamma_{n-k}(\tau) \dot{\lambda}_k(\tau) \right]. \tag{12}$$

The left-hand side of Eq. (12) is $\sim O(1)$, whereas the right-hand side features terms of orders up to $\sim O(\tau^{n-1})$, which cancel out each other and would be wasteful to compute. In order to streamline the discussion to follow, it is convenient to denote by x° the term of order zero in the asymptotic expansion of $x(\tau)$ as $\tau \to \infty$: $x(\tau) \sim x^\circ + O(\tau) + O(\tau^2) + \cdots$. Of course, $\dot{x}^\circ$ indicates the zeroth-order term of $\dot{x}(\tau)$ and not the derivative of the zeroth-order term, which would otherwise vanish. Equations (10) and (12) hold verbatim for the values of the constant terms in the asymptotic expansions of $\gamma_n(\tau)$ and $\dot{\gamma}_n(\tau)$, γ_n° and $\dot{\gamma}_n^\circ$—the latter coinciding with the finite $\tau \to \infty$ limit—in terms of the λ°'s and $\dot{\lambda}^\circ$'s:

$$\begin{aligned} \gamma_n^\circ &= \lambda_n^\circ - \sum_{k=1}^{n-1} \frac{n-k}{n} \gamma_{n-k}^\circ \lambda_k^\circ, \\ \dot{\gamma}_n^\circ &= \dot{\lambda}_n^\circ - \sum_{k=1}^{n-1} \frac{n-k}{n} (\dot{\gamma}_{n-k}^\circ \lambda_k^\circ + \gamma_{n-k}^\circ \dot{\lambda}_k^\circ). \end{aligned} \tag{13}$$

The asymptotic ($\tau \to \infty$) behavior of a function of a real argument, such as $\lambda_n(\tau)$, is determined by the analytical properties of its Laplace transform,

$$\bar{\lambda}_n(z) \doteq \int_0^\infty \lambda_n(\tau) e^{-z\tau} d\tau, \tag{14}$$

near the origin, $z = 0$. In fact, as the Laplace transform of τ^n is $n!/z^{n+1}$, λ_n° and $\dot{\lambda}_n^\circ$ are the coefficients of order -1 and -2, respectively, of the Laurent expansion of $\bar{\lambda}_n(z)$ around the origin. In order to evaluate Eq. (14), we note that the multiple integral in Eq. (7) is the convolution $1 * e^{-\mathcal{E}_{k_{n-1}}\tau} \cdots * e^{-\mathcal{E}_{k_1}\tau} * 1$, whose Laplace transform is $1/(\mathcal{E}_{k_{n-1}} + z) \cdots / (\mathcal{E}_{k_1} + z)/z^2$. Therefore,

$$\bar{\lambda}_n(z) = \frac{1}{z^2} G_n(z), \tag{15}$$

where $G_1(z) = \mathcal{W}_{00}$ and for $n > 1$ one has

$$G_n(z) = \sum_{k_1 \cdots k_{n-1}} \frac{\mathcal{W}_{0k_{n-1}} \mathcal{W}_{k_{n-1}k_{n-2}} \cdots \mathcal{W}_{k_1 0}}{(\mathcal{E}_{k_{n-1}} + z) \cdots (\mathcal{E}_{k_1} + z)}. \tag{16}$$

We conclude that λ_n° and $\dot{\lambda}_n^\circ$ are the coefficients of order one and zero, respectively, in the Laurent expansion of $G_n(z)$ around the origin. For future reference, it is expedient to designate the term where no ground-state contributions to the sum in Eq. (16) occur as

$$g_n(z) = {\sum_{k_1 k_2 \cdots k_{n-1}}}' \frac{\mathcal{W}_{0k_{n-1}} \mathcal{W}_{k_{n-1}k_{n-2}} \cdots \mathcal{W}_{k_1 0}}{(\mathcal{E}_{k_{n-1}} + z) \cdots (\mathcal{E}_{k_1} + z)}, \tag{17}$$

where $\sum'$ indicates a multiple sum excluding all the terms where at least one of the indices vanish ($k_i = 0$).

The analytical behavior of the various terms appearing in Eq. (16) is determined by the number of times the ground state ($k_i = 0$) occurs in each one of them, each time raising the order of the pole at $z = 0$ by one unit. Let us depict any such term as a sequence of $n + 1$ boxes, each labeled by a summation index k_i, with the two indices at the extrema being kept equal to zero, $k_0 = k_n = 0$:

$$\boxed{0 \mid k_1 \mid k_2 \mid \cdots \mid k_{n-1} \mid 0}.$$

We can now partition Eq. (16) into partial sums, each one characterized by the number ℓ of vanishing k_i indices ($\ell = 0, \ldots, n-1$). Any term of a partial sum is the ratio between the product of $\ell + 1$ g's [Eq. (17)], which is a regular function as $z \to 0$, and z^ℓ. For instance, one term of the $\ell = 2$ partial sum could look like

$$\underbrace{\boxed{0 \mid \cdots \mid 0}}_{g_{n_1}} \underbrace{\boxed{\cdots \mid \cdots}}_{g_{n_2}} \underbrace{\boxed{0 \mid \cdots \mid 0}}_{g_{n_3}} /z^2,$$

with $n_1 + n_2 + n_3 = n$. In the diagram above, as well as in much of the text to follow, the argument of $g_n(z)$ is suppressed for notational convenience. Some of the n_i's in the product may be equal to each other. The maximum order n_k appearing in the partial sum, i.e., the number of arguments of the multivariate polynomial representing the sum, corresponds to the term where the ℓ initial (or final) k_i indices in Eq. (16) vanish. For instance, in the $\ell = 2$ case examined above, this would be represented by the two diagrams

$$\underbrace{\boxed{0 \mid 0}}_{g_1} \underbrace{\boxed{0 \mid \cdots \mid \cdots}}_{g_1} \underbrace{\boxed{\cdots \mid \cdots \mid 0}}_{g_{n-2}} /z^2,$$

and

$$\underbrace{\boxed{0 \mid \cdots}}_{g_{n-2}} \underbrace{\boxed{\cdots \mid \cdots}}_{g_1} \underbrace{\boxed{\cdots \mid 0 \mid 0}}_{g_1} /z^2,$$

both corresponding to the contribution $(g_1)^2 g_{n-2}$. In the general case, diagrams of this kind give rise to the contribution $(g_1)^\ell g_{n-\ell}$. The most general contribution to the ℓth partial sum is thus a multivariate monomial in the g's of the form

$$C(\boldsymbol{g}_{n-l}, \boldsymbol{j}_{n-l}) = (g_1)^{j_1} (g_2)^{j_2} \cdots (g_{n-\ell})^{j_{n-\ell}}, \tag{18}$$

where $\boldsymbol{g}_{n-\ell} = \{g_1, g_2, \ldots, g_{n-\ell}\}$ and $\boldsymbol{j}_{n-l} = \{j_1, j_2, \ldots, j_{n-\ell}\}$ is an array of $n - \ell$ *non-negative* integers satisfying the constraints

$$\begin{aligned} j_1 + j_2 + \cdots j_{n-\ell} &= \ell + 1, \\ j_1 + 2j_2 + \cdots (n-\ell) j_{n-\ell} &= n, \end{aligned} \tag{19}$$

and one or more of the j_k's may vanish. The multiplicity $N(\boldsymbol{j}_{n-l})$ of the $C(\boldsymbol{g}_{n-l}, \boldsymbol{j}_{n-l})$ monomial is equal to the number of ways a set of $\ell + 1$ elements grouped in subsets of $\{j_1, j_2, \ldots, j_{n-\ell}\}$ equal elements (some of the j's may vanish), can be partitioned into $\ell + 1$ boxes. Simple combinatorics gives

$$N(\boldsymbol{j}_{n-\ell}) = \frac{(\ell+1)!}{j_1! j_2! \cdots j_{n-\ell}!}. \tag{20}$$

We conclude that Eq. (16) can be put into the form

$$G_n(z) = \sum_{\ell=0}^{n-1} \frac{1}{z^\ell} \sum_{j_1 j_2 \cdots j_{n-\ell}} \frac{(\ell+1)!}{j_1! j_2! \cdots j_{n-\ell}!} (g_1)^{j_1} (g_2)^{j_2} \cdots (g_{n-\ell})^{j_{n-\ell}}, \tag{21}$$

where the multiple sum is restricted to the j's subject to the constraints in Eqs. (19). This multiple sum coincides with the definition of the *ordinary Bell polynomial* [8] of order $(n, \ell + 1)$, $\mathcal{B}_{n,\ell+1}(\boldsymbol{g}_{n-\ell})$ [9]. Equations (14)–(16) can thus be cast into the form

$$G_n(z) = \sum_{l=1}^{n} z^{-l+1} \mathcal{B}_{nl}(\mathbf{g}_{n-l+1}(z)). \tag{22}$$

By extracting from the Laurent expansion of Eq. (22) the terms of order one and zero and equating them to λ_n°, and $\dot{\lambda}_n^\circ$, respectively, as discussed before, one gets

$$\begin{aligned} \lambda_n^\circ &= \sum_{l=1}^{n} \frac{1}{l!} \mathcal{B}_{nl}^{(l)}, \\ \dot{\lambda}_n^\circ &= \sum_{l=1}^{n} \frac{1}{(l-1)!} \mathcal{B}_{nl}^{(l-1)}, \end{aligned} \tag{23}$$

where $\mathcal{B}_{nl}^{(k)} = \frac{d^k}{dz^k} \mathcal{B}_{nl}(\mathbf{g}_{n-l+1}(z))|_{z=0}$. These derivatives can be expressed as linear combinations of multiple derivatives of the g_n's, $g_n^{(k)} = \frac{d^k}{dz^k} g_n(z)|_{z=0}$, using a multivariate extension of the Faà di Bruno formula [10], involving again Bell's polynomials. Note that, contrary to the g_n's, which are to be understood as functions of z, the various $g_n^{(k)}$'s are constants. In particular, $g_n^{(0)} = g_n(0)$. In practice, the coefficients of these linear combinations quickly become so complex that they can only be handled through symbolic manipulation systems, which would be more profitably used to obtain the result by direct differentiation. In any case, the derivatives of the g_n's can be expressed in terms of the complete homogeneous symmetric

polynomials [11] of the inverse excitation energies, $X_n = \mathcal{E}_n^{-1}$,

$$h_l(X_1,\ldots,X_n) = \sum_{1\leqslant k_1\cdots k_n\leqslant l} X_{k_1}\cdots X_{k_n} = \frac{1}{l!}\frac{d^l}{dz^l}\left(\frac{1}{1-zX_1}\cdots\frac{1}{1-zX_n}\right)_{z=0}. \tag{24}$$

We have therefore

$$\begin{aligned} g_n^{(l)} &= \left.\frac{d^l}{dz^l}g_n(z)\right|_{z=0} = \left.\frac{d^l}{dz^l}\sum_{k_1k_2\cdots k_{n-1}}{}' \frac{\mathcal{W}_{0k_{n-1}}\mathcal{W}_{k_{n-1}k_{n-2}}\cdots\mathcal{W}_{k_10}}{(\mathcal{E}_{k_{n-1}}+z)\cdots(\mathcal{E}_{k_1}+z)}\right|_{z=0} \\ &= l!(-)^{n-1}\sum_{k_1k_2\cdots k_{n-1}}{}' \frac{\mathcal{W}_{0k_{n-1}}\mathcal{W}_{k_{n-1}k_{n-2}}\cdots\mathcal{W}_{k_10}}{\mathcal{E}_{k_{n-1}}\cdots\mathcal{E}_{k_1}} h_l\left(\mathcal{E}_{k_1}^{-1},\ldots,\mathcal{E}_{k_{n-1}}^{-1}\right). \end{aligned} \tag{25}$$

The box below [Eqs. (26)] summarizes the formulas for the calculation of the various terms in the perturbative expansion of the GS energy of the Hamiltonian [Eq. (2)] to arbitrary order [Eqs. (11), (13), and (23)]:

$$\boxed{\begin{array}{lll} E_0 = \mathcal{E}_0 + \varepsilon_1 + \cdots \varepsilon_n + \cdots, & \gamma_n^\circ = \lambda_n^\circ - \sum_{k=1}^{n-1}\frac{n-k}{n}\gamma_{n-k}^\circ\lambda_k^\circ, & \lambda_n^\circ = \sum_{l=1}^n \frac{1}{l!}\mathcal{B}_{nl}^{(l)}, \\ \varepsilon_n = (-)^{n+1}\dot\gamma_n^\circ, & \dot\gamma_n^\circ = \dot\lambda_n^\circ - \sum_{k=1}^{n-1}\frac{n-k}{n}\left(\dot\gamma_{n-k}^\circ\lambda_k^\circ + \gamma_{n-k}^\circ\dot\lambda_k^\circ\right), & \dot\lambda_n^\circ = \sum_{l=1}^n \frac{1}{(l-1)!}\mathcal{B}_{nl}^{(l-1)}. \end{array}} \tag{26}$$

These equations are easily implemented in any symbolic manipulation package. A simple MATHEMATICA [12] code, named TUMITURBI.NB, is available as Supplemental Material [13].

$$\begin{aligned} \varepsilon_1 =& g_1, \\ \varepsilon_2 =& -g_2, \\ \varepsilon_3 =& g_3 + g_1g_2', \\ \varepsilon_4 =& -g_4 - g_2g_2' - g_1g_3' - \frac{1}{2}g_1^2g_2'', \\ \varepsilon_5 =& g_5 + g_3g_2' + g_1(g_2')^2 + g_2g_3' + g_1g_4' \\ &+ g_1g_2g_2'' + \frac{1}{2}g_1^2g_3'' + \frac{1}{6}g_1^3g_2^{(3)}, \\ \varepsilon_6 =& -g_6 - g_4g_2' - g_2(g_2')^2 - g_3g_3' - 2g_1g_2'g_3' \\ &- g_2g_4' - g_1g_5' - \frac{1}{2}g_2^2g_2'' - g_1g_3g_2'' \\ &- \frac{3}{2}g_1^2g_2'g_2'' - g_1g_2g_3'' - \frac{1}{2}g_1^2g_4'' \\ &- \frac{1}{2}g_1^2g_2g_2^{(3)} - \frac{1}{6}g_1^3g_3^{(3)} - \frac{1}{24}g_1^4g_2^{(4)}. \end{aligned} \tag{27}$$

The box above [Eqs. (27)] reports the first six terms in the perturbative expansion of the GS energy, as obtained from this code. Note the difference between $g_l^k = (g_l)^k$ and $g_l^{(k)} = \frac{d^kg_l}{dz^k}$. These results are in agreement with those obtained in Ref. [14] from a different method based on gauge invariance. TUMITURBI.NB also provides the explicit expressions for the perturbative corrections in terms of the familiar sums over excited states, in a slightly awkward, but perfectly recognizable, form.

III. THE CLASSICAL-QUANTUM MAPPING

In order to proceed further and establish a stochastic interpretation of the perturbative series [Eq. (11)] we consider a classical system of N interacting particles, whose coordinates are denoted by $\boldsymbol{R} = \{\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots, \boldsymbol{r}_N\} \in \mathbb{R}^{3N}$ and whose dynamics is described by a random walk satisfying the overdamped Langevin equation

$$\begin{aligned} \boldsymbol{R}_{n+1} &= \boldsymbol{R}_n + \epsilon\boldsymbol{\mathcal{F}}(\boldsymbol{R}_n) + d\boldsymbol{W}_n, \\ \boldsymbol{\mathcal{F}} &= -\frac{\partial\mathcal{U}(\boldsymbol{R})}{\partial\boldsymbol{R}}, \end{aligned} \tag{28}$$

where $\mathcal{U}(\boldsymbol{R})$ is a many-body potential, $d\boldsymbol{W}_n$ is the differential of a Wiener process with variance $\langle(d\boldsymbol{W}_n)^2\rangle = 2\epsilon$, and the subscript n is a discrete-time index corresponding to a discretization step ϵ. In the continuous ($\epsilon \to 0$) limit, the probability density for the walker $\boldsymbol{R}$, $\mathsf{P}(\boldsymbol{R},\tau)$, satisfies the Fokker-Planck (FP) equation [3,4]

$$\frac{\partial\mathsf{P}(\boldsymbol{R},\tau)}{\partial\tau} = \frac{\partial^2\mathsf{P}(\boldsymbol{R},\tau)}{\partial\boldsymbol{R}^2} - \frac{\partial}{\partial\boldsymbol{R}}\cdot(\boldsymbol{\mathcal{F}}(\boldsymbol{R})\mathsf{P}(\boldsymbol{R},\tau)). \tag{29}$$

It is easily checked that $\mathsf{P}^\circ(\boldsymbol{R}) \propto e^{-\mathcal{U}(\boldsymbol{R})}$ is a stationary solution of the FP equation [Eq. (29)]. We will shortly see that, under rather general conditions, this stationary solution is unique. To this end, let us introduce two auxiliary *wave functions* defined as

$$\Phi_0(\boldsymbol{R}) = \sqrt{\mathsf{P}^\circ(\boldsymbol{R})} \propto e^{-\mathcal{U}(\boldsymbol{R})/2}, \tag{30}$$

$$\Phi(\boldsymbol{R},\tau) = \mathsf{P}(\boldsymbol{R},\tau)/\Phi_0(\boldsymbol{R}). \tag{31}$$

It is easy to verify that $\Phi(\boldsymbol{R},\tau)$ satisfies the (imaginary-) time-dependent Schrödinger equation

$$\frac{\partial\Phi(\boldsymbol{R},\tau)}{\partial\tau} = -\widehat{\mathcal{H}}\Phi(\boldsymbol{R},\tau), \tag{32}$$

where

$$\widehat{\mathcal{H}} = -\frac{\partial^2}{\partial\boldsymbol{R}^2} + \mathcal{V}(\boldsymbol{R}), \tag{33}$$

and

$$\mathcal{V}(\boldsymbol{R}) = \frac{1}{4}\mathcal{F}(\boldsymbol{R})^2 - \frac{1}{2}\mathcal{U}''(\boldsymbol{R}) = \frac{\Phi_0''(\boldsymbol{R})}{\Phi_0(\boldsymbol{R})}, \tag{34}$$

where a double prime indicates a second derivative (Laplacian): $F''(\boldsymbol{R}) = \frac{\partial^2}{\partial \boldsymbol{R}^2} F(\boldsymbol{R})$. Equations (33) and (34) imply that Φ_0 [Eq. (30)] is an eigenfunction of the Hamiltonian [Eq. (33)] with zero eigenvalue. If $\mathcal{U}(\boldsymbol{R})$ [Eq. (28)] is everywhere finite, then $\mathsf{P}^\circ(\boldsymbol{R})$ and $\Phi_0(\boldsymbol{R})$ are nodeless, and the latter is the nondegenerate ground state of the Hamiltonian [Eq. (33)] [15]. As a consequence, all the excited states have strictly positive energies, and therefore $\lim_{\tau\to\infty} \Phi(\boldsymbol{R},\tau) \propto \Phi_0(\boldsymbol{R})$ and $\lim_{\tau\to\infty} \mathsf{P}(\boldsymbol{R},\tau) = \mathsf{P}^\circ(\boldsymbol{R})$, irrespective of the initial conditions, i.e., $\mathsf{P}^\circ(\boldsymbol{R})$ is the unique equilibrium solution of the FP equation [Eq. (29)].

The FP equation (29) is first order in time, reflecting the Markovian character of the Langevin process [Eq. (28)]. This entails that its solution $\mathsf{P}(\boldsymbol{R},\tau)$ is uniquely determined by the corresponding initial condition $\mathsf{P}(\boldsymbol{R},0)$. Linearity in turn implies that $\mathsf{P}(\boldsymbol{R},\tau)$ is the convolution of $\mathsf{P}(\boldsymbol{R},0)$ with a Green's function $\Pi(\boldsymbol{R},\boldsymbol{R}';\tau)$, which is to be interpreted as the conditional probability density for the walker to be found at position $\boldsymbol{R}$ at time τ, given that it was found at position $\boldsymbol{R}'$ at time 0:

$$\mathsf{P}(\boldsymbol{R},\tau) = \int \Pi(\boldsymbol{R},\boldsymbol{R}';\tau)\mathsf{P}(\boldsymbol{R}',0)d\boldsymbol{R}'. \tag{35}$$

A similar relation holds for the propagation of the associated quantum wave function,

$$\Phi(\boldsymbol{R},\tau) = \int \mathcal{G}(\boldsymbol{R},\boldsymbol{R}';\tau)\Phi(\boldsymbol{R}',0)d\boldsymbol{R}', \tag{36}$$

where $\mathcal{G}(\boldsymbol{R},\boldsymbol{R}';\tau) = \langle \boldsymbol{R}|e^{-\widehat{\mathcal{H}}\tau}|\boldsymbol{R}'\rangle$ is the imaginary-time propagator of the auxiliary quantum system. By inserting Eq. (31) into Eq. (36), one gets

$$\Pi(\boldsymbol{R},\boldsymbol{R}';\tau) = \Phi^\circ(\boldsymbol{R})\mathcal{G}(\boldsymbol{R},\boldsymbol{R}';\tau)/\Phi^\circ(\boldsymbol{R}'). \tag{37}$$

If the process is stationary, the marginal probability density for the walker's position is independent of time, $\mathsf{P}(\boldsymbol{R},\tau) = \mathsf{P}^\circ(\boldsymbol{R})$, and the time average of any function of the walker's coordinates, $\mathcal{A}(\boldsymbol{R})$,

$$\bar{\mathcal{A}}_\mathcal{T} = \frac{1}{\mathcal{T}}\int_0^\mathcal{T} \mathcal{A}(\boldsymbol{R}(\tau))d\tau, \tag{38}$$

is a stochastic variable whose expectation is

$$\langle \bar{\mathcal{A}}_\mathcal{T}\rangle_{\mathrm{RW}} = \langle \mathcal{A}\rangle \doteq \int \mathcal{A}(\boldsymbol{R})\mathsf{P}^\circ(\boldsymbol{R})d\boldsymbol{R} \equiv \langle \Phi_0|\widehat{\mathcal{A}}|\Phi_0\rangle, \tag{39}$$

and whose variance is

$$\begin{aligned}\mathrm{var}(\bar{\mathcal{A}}_\mathcal{T}) &= \frac{1}{\mathcal{T}^2}\left\langle \left(\int_0^\mathcal{T} \Delta\mathcal{A}(\tau)d\tau\right)^2\right\rangle_{\mathrm{RW}} \\ &= \frac{2}{\mathcal{T}}\int_0^\mathcal{T} \langle \Delta\mathcal{A}(\tau)\Delta\mathcal{A}(0)\rangle_{\mathrm{RW}}\left(1-\frac{\tau}{\mathcal{T}}\right)d\tau \\ &\sim \frac{2}{\mathcal{T}}\int_0^\infty \langle \Delta\mathcal{A}(\tau)\Delta\mathcal{A}(0)\rangle_{\mathrm{RW}}d\tau,\end{aligned} \tag{40}$$

where

$$\Delta\mathcal{A}(\tau) = \mathcal{A}(\boldsymbol{R}(\tau)) - \langle \mathcal{A}\rangle, \tag{41}$$

$\langle\cdot\rangle_{\mathrm{RW}}$ indicates an equilibrium average over the random walk, and the last relation in Eq. (40) holds in the $\mathcal{T}\to\infty$ limit when $\int_0^\infty \langle \Delta\mathcal{A}(\tau)\Delta\mathcal{A}(0)\rangle_{\mathrm{RW}}\tau d\tau < +\infty$. Notice the similarity between the expression for the variance for the time average of a function of the walker's coordinates [Eq. (40)] and the Einstein-Helfand expression for transport coefficients [16–19]. Equation (40), as well as the related equivalence between the Green-Kubo and Einstein-Helfand expressions for transport coefficients, is a direct consequence of the fact that the variance of the average of N of stochastic variables [the integral in Eq. (38)] is equal to the sum of the all the elements of the covariance matrix divided by N^2, which for independent equally distributed variables results in the familiar law of large numbers.

If the process is stationary, the joint probability density for the walker to be found at positions $\boldsymbol{R}_1, \boldsymbol{R}_2, \cdots, \boldsymbol{R}_n$ at times $\tau_1, \tau_2, \cdots, \tau_n$ is

$$\begin{aligned}\mathsf{P}_n(\boldsymbol{R}_n,\tau_n;\boldsymbol{R}_{n-1}\tau_{n-1};\cdots;\boldsymbol{R}_1,\tau_1) &= \Pi(\boldsymbol{R}_n,\boldsymbol{R}_{n-1};\tau_n-\tau_{n-1}) \\ &\times \Pi(\boldsymbol{R}_{n-1},\boldsymbol{R}_{n-2};\tau_{n-1}-\tau_{n-2})\times\cdots\Pi(\boldsymbol{R}_2,\boldsymbol{R}_1;\tau_2-\tau_1)\mathsf{P}^\circ(\boldsymbol{R}_1).\end{aligned} \tag{42}$$

The time correlation function of a function of the local coordinates $\mathcal{A}(\boldsymbol{R})$ reads therefore

$$\begin{aligned}\langle \Delta\mathcal{A}(\tau)\Delta\mathcal{A}(0)\rangle_{\mathrm{RW}} &= \int \mathsf{P}_2(\boldsymbol{R}_2,\tau;\boldsymbol{R}_1,0)\Delta\mathcal{A}(\boldsymbol{R}_2)\Delta\mathcal{A}(\boldsymbol{R}_1)d\boldsymbol{R}_2d\boldsymbol{R}_2 \\ &= \int \Phi_0(\boldsymbol{R}_2)\Phi_0(\boldsymbol{R}_1)\mathcal{G}(\boldsymbol{R}_2,\boldsymbol{R}_1;\tau)\Delta\mathcal{A}(\boldsymbol{R}_2)\Delta\mathcal{A}(\boldsymbol{R}_1)d\boldsymbol{R}_1d\boldsymbol{R}_2 \\ &= \sum_{n>0}|\mathcal{A}_{0n}|^2e^{-\mathcal{E}_n\tau},\end{aligned} \tag{43}$$

where Φ_n and $\mathcal{E}_n$ indicate the eigenpair of the nth excited state of the Hamiltonian, Eq. (33), $\mathcal{A}_{0n} = \langle\Phi_0|\widehat{\mathcal{A}}|\Phi_n\rangle$, and the GS energy $\mathcal{E}_0$ is assumed to vanish. By combining Eq. (40) with Eq. (43), we arrive at an expression for the variance of the time

average of a function of the walker's coordinates in terms of a spectral sum for the associated quantum system:

$$\mathrm{var}(\bar{\mathcal{A}}_{\mathcal{T}}) \sim \frac{2}{\mathcal{T}} \sum_{n>0} \frac{|\mathcal{A}_{0n}|^2}{\mathcal{E}_n}. \tag{44}$$

IV. STOCHASTIC PERTURBATION THEORY

The approach to perturbation theory presented in Sec. II applies to any Hamiltonian that can be split as in Eq. (2). When both the complete and unperturbed Hamiltonians of a continuous, nonrelativistic, N-body system are sums of a kinetic and a local, possibly nonseparable, potential term, the GS wave functions are nodeless [15,20] and the unperturbed quantum problem can be mapped onto a classical diffusion one, such that the perturbative expansion can be given a nice and insightful stochastic interpretation.

Let us denote by $\boldsymbol{R} = \{\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots, \boldsymbol{r}_N\} \in \mathbb{R}^{3N}$ the coordinates of the system and by

$$\widehat{H} = -\frac{1}{2}\frac{\partial^2}{\partial \boldsymbol{R}^2} + V(\boldsymbol{R}),$$

$$\widehat{\mathcal{H}} = -\frac{1}{2}\frac{\partial^2}{\partial \boldsymbol{R}^2} + \mathcal{V}(\boldsymbol{R}), \tag{45}$$
$$\mathcal{W}(\boldsymbol{R}) = V(\boldsymbol{R}) - \mathcal{V}(\boldsymbol{R}),$$

the complete and unperturbed Hamiltonians, respectively. The eigenvalue equation (1) gives

$$\mathcal{V}(\boldsymbol{R}) = \mathcal{E}_0 + \frac{1}{2}\frac{\Phi_0''(\boldsymbol{R})}{\Phi_0(\boldsymbol{R})}, \tag{46}$$

where Φ_0 is the unperturbed GS wave function. If one assumes $\mathcal{E}_0 = 0$, then

$$\begin{aligned}\mathcal{W}(\boldsymbol{R}) &= -\frac{1}{2}\frac{\Phi_0''(\boldsymbol{R})}{\Phi_0(\boldsymbol{R})} + V(\boldsymbol{R}) \\ &= \left(\widehat{H}\Phi_0(\boldsymbol{R})\right)\Big/\Phi_0(\boldsymbol{R}).\end{aligned} \tag{47}$$

In the quantum Monte Carlo parlance, the perturbing potential $\mathcal{W}(\boldsymbol{R})$ [Eq. (47)] is usually dubbed the *local energy* [21].

A stochastic interpretation of the perturbative expansion is obtained by replacing the multiple sum over intermediate Hamiltonian eigenstates leading from Eq. (6) to (7) with a multiple integral over intermediate positions, reading

$$\begin{aligned}\lambda_n(\tau) &= \int_0^\tau d\tau_n \int_0^{\tau_n} d\tau_{n-1} \cdots \int_0^{\tau_2} d\tau_1 \int d\boldsymbol{R}_n d\boldsymbol{R}_{n-1} \cdots d\boldsymbol{R}_1 \Phi_0(\boldsymbol{R}_n)\mathcal{W}(\boldsymbol{R}_n)\mathcal{W}(\boldsymbol{R}_{n-1}) \cdots \mathcal{W}(\boldsymbol{R}_1) \\ &\quad \times \mathcal{G}(\boldsymbol{R}_n, \boldsymbol{R}_{n-1}; \tau_n - \tau_{n-1})\mathcal{G}(\boldsymbol{R}_{n-1}, \boldsymbol{R}_{n-2}; \tau_{n-1} - \tau_{n-2}) \cdots \mathcal{G}(\boldsymbol{R}_2, \boldsymbol{R}_1; \tau_2 - \tau_1)\Phi_0(\boldsymbol{R}_1) \\ &= \int_0^\tau d\tau_n \int_0^{\tau_n} d\tau_{n-1} \cdots \int_0^{\tau_2} d\tau_1 \int d\boldsymbol{R}_n d\boldsymbol{R}_{n-1} \cdots d\boldsymbol{R}_1 \mathcal{W}(\boldsymbol{R}_n)\mathcal{W}(\boldsymbol{R}_{n-1}) \cdots \mathcal{W}(\boldsymbol{R}_1) \\ &\quad \times \mathsf{P}_n(\boldsymbol{R}_n, \tau_n; \boldsymbol{R}_{n-1}\tau_{n-1}; \cdots; \boldsymbol{R}_1, \tau_1) \\ &= \int_0^\tau d\tau_n \int_0^{\tau_n} d\tau_{n-1} \cdots \int_0^{\tau_2} d\tau_1 \langle \mathcal{W}(\tau_n)\mathcal{W}(\tau_{n-1}) \cdots \mathcal{W}(\tau_1)\rangle_{\mathrm{RW}} \\ &= \frac{1}{n!}\langle \mathcal{S}(\tau)^n \rangle_{\mathrm{RW}},\end{aligned} \tag{48}$$

where $\mathcal{S}(\tau) = \int_0^\tau \mathcal{W}(\tau')d\tau'$ can be thought of as an effective action [22]. The μ's, $\mu_n(\tau) = n!\lambda_n(\tau)$ [Eq. (6)], are thus the (raw) moments of the effective action, and the various perturbative corrections in Eq. (11) are derivatives of the corresponding cumulants. When τ is larger than the local-energy ($\mathcal{W}$) autocorrelation time $\tau_{\mathcal{W}}$, $\mathcal{S}(\tau)$ is the sum of $\mathcal{N} \approx \tau/\tau_{\mathcal{W}}$ quasi-independent stochastic variables, so that its cumulants are proportional to $\mathcal{N}$, and therefore to τ, making the large-time limit of their derivatives well defined.

V. REPTATION QUANTUM MONTE CARLO

The most basic of all the stochastic approaches to quantum mechanics is likely *variational quantum Monte Carlo* (VMC), whereby one aims to estimate the GS energy of a system as the expectation value of the Hamiltonian with respect to a suitably identified approximate wave function $\Phi_0(\boldsymbol{R})$,

$$\begin{aligned}E_0 &\approx \langle \Phi_0 | \widehat{H} | \Phi_0 \rangle \\ &\doteq \int \mathcal{W}(\boldsymbol{R})\Phi_0(\boldsymbol{R})^2 d\boldsymbol{R},\end{aligned} \tag{49}$$

where $\mathcal{W}(\boldsymbol{R})$ is given by Eq. (47). This is conveniently achieved by sampling $\mathcal{W}(\boldsymbol{R})$ along a random walk generated by the Langevin equation (28), with $\mathcal{U}(\boldsymbol{R}) = -2\ln\Phi_0(\boldsymbol{R})$, using Eqs. (39) and (40) with $\mathcal{A} = \mathcal{W}$.

The classical-quantum mapping presented in Sec. III permits to interpret Φ_0 as the GS wave function of the auxiliary Hamiltonian $\widehat{\mathcal{H}}$ associated with the FP equation for the Langevin random walk. Of course, if Φ_0 coincided with the exact wave function of our quantum system, $\widehat{\mathcal{H}}$ would coincide with the exact Hamiltonian $\widehat{H}$. If this is not the case, it would be reasonable to treat the difference $\widehat{H} - \widehat{\mathcal{H}} = \widehat{\mathcal{W}}$ by perturbation theory. According to Eqs. (10), (11), and (48), the first few corrections to the unperturbed ($\mathcal{E}_0 = 0$) energy read

$$\varepsilon_1 = \langle \mathcal{W} \rangle_{\mathrm{RW}}, \tag{50}$$

$$\varepsilon_2 = -\int_0^\infty \langle \Delta\mathcal{W}(\tau)\Delta\mathcal{W}(0)\rangle_{\mathrm{RW}} d\tau \tag{51}$$

$$\doteq -\langle (\Delta\mathcal{W})^2 \rangle_{\mathrm{RW}} \tau_{\mathcal{W}}, \tag{52}$$

where $\Delta\mathcal{W}$ is defined in analogy with Eq. (41) and the local-energy autocorrelation time $\tau_{\mathcal{W}}$ is actually defined by Eqs. (51) and (52). The first-order correction [Eq. (50)] coincides with the VMC estimate of the GS energy. Equation (52) states that the information contained in the local-energy time series generated in a regular VMC simulation is sufficient to evaluate the second- (and, actually, higher-) order correction(s) to the VMC estimate.

The stochastic interpretation of the higher-order terms [Eqs. (5) and (48)] allows one to formally sum the perturbative series up to infinite order as the expected value over the random walk of the exponential of the negative of the action:

$$\mathcal{Z}(\tau) = \sum_{n=0}^{\infty} \frac{(-)^n}{n!} \langle \mathcal{S}(\tau)^n \rangle_{\mathrm{RW}} \tag{53}$$

$$= \langle e^{-\mathcal{S}(\tau)} \rangle_{\mathrm{RW}}. \tag{54}$$

The expression given by Eq. (3) for the GS energy reads therefore

$$E_0 \sim \frac{\langle \mathcal{W}(\tau) e^{-\mathcal{S}(\tau)} \rangle_{\mathrm{RW}}}{\langle e^{-\mathcal{S}(\tau)} \rangle_{\mathrm{RW}}}. \tag{55}$$

Neglecting action fluctuations, Eq. (55) reduces to the usual VMC expression for the energy. These fluctuations could be accounted for by weighting the local energy with $e^{-\mathcal{S}(\tau)}$, resulting in the *pure-diffusion quantum Monte Carlo* scheme of Ref. [23]. The exponential dependence of the weights on the action and the extensive character of the latter, however, make this scheme unfit but for systems of very small size and not very efficient otherwise. Similar approaches, all derived from a Feynman-Kac expression for the $\mathcal{Z}$ function in Eq. (3), are the *variational path-integral* method of Ref. [24], later rebranded as *path-integral ground state* [25], and RQMC [4,5]. In all these methods, the effects of the weights are accounted for by sampling the space of random walks of length τ, $\boldsymbol{X}(\tau) = \{\boldsymbol{R}(\epsilon), \boldsymbol{R}(2\epsilon), \ldots, \boldsymbol{R}(\tau = n\epsilon)\}$ according to a Metropolis algorithm [26]. The distinctive feature of RQMC is the way Monte Carlo moves are generated by letting the random walk (the *reptile*) creep back and forth for a certain time according to the Langevin equation (28) and accepted or rejected according to a Metropolis test on the variation of the effective action determined by the move. Besides the energy, RQMC allows for an unbiased estimate of general local observables, as well as of their static and dynamic (in imaginary time) response functions. The algorithm is explained in full detail elsewhere [4,5].

VI. CONCLUSIONS

The work presented in this paper is made of two independent parts, whose main link is their relation to the development of reptation quantum Monte Carlo in the late nineties. Indeed, this development was motivated by the observation that the leading correction to the variational estimate of a ground-state energy is determined by the Kubo-like formula given by Eq. (51) and by the difficulty to generalize it to higher orders in any useful manner. Sometimes, insurmountable difficulties are fortunate, for RQMC has proven to be much more powerful than any approximate perturbative schemes ever could: Besides the intrinsically approximate character of perturbation theory, the main numerical limitation to a stochastic approach to it is the increasing numerical noise affecting the estimate of the action moments for increasing order and the ill-conditioned nature of the expression of cumulants in terms of moments [Eqs. (9) and (10)] due to sign alternation. The first part of this work, Sec. II, is to a large extent unrelated from the second, but for the fact that I have long been wondering how Eq. (3), which is the starting point of RQMC and of many other quantum stochastic simulation methods, could be used to streamline the derivation of Rayleigh-Schrödinger perturbation theory. I hope the present paper provides an answer to this question.

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