Non-Gaussian influence functional for quantum systems

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We consider the quantum paths (in Euclidean time) through a space of N multiparticle states, and we derive the influence functional for a subset of m primary states in this space. The influence functional results from integrating out the occupation of the N-m nonprimary or bath states holding fixed the time-dependent occupation path through the primary states. The division into bath states and primary states is completely general in principle, though in practice, physical considerations will guide the choice of partitioning. The exact influence functional is nonlocal in time and very complicated in form. We argue, however, by a variational calculation that a simplified approximate functional can be constructed which is very accurate. Unlike the standard Gaussian influence functionals which are inapplicable for processes involving the large amplitude fluctuations of charge transfer and fermionic exchange, the influence functionals described herein are appropriate for models of these processes.

I. INTRODUCTION

Path integral methods provide a most convenient theoretical approach when considering quantum mechanical systems coupled to a bath. Central to this approach is the concept of an influence functional. A standard model is the Gaussian influence functional that results from integrating out a bath of harmonic oscillators which are linearly coupled to the quantum system under investigation. With judicious choices of dynamical variables and couplings, this model can be made very accurate even for highly nonlinear systems. A recent example is the description of excess electrons in liquids where the liquid is treated as a bath in which the density fields fluctuate harmonically.

It appears, however, that the Gaussian or harmonic model cannot describe the influence of a fluctuating bath when this subsystem exchanges particles with the primary system under investigation. The possibility of exchange is important to chemistry involving charge transfer and bonding. Therefore, it would seem advantageous to develop a model for influence functionals that can incorporate the effects of exchange. As a first step in this direction, we present in this paper the analysis of an influence functional obtained from a somewhat different perspective than has been considered before.

In particular, we imagine a space of N multiparticle states and deduce the influence functional for a set of m primary states in this Hilbert space. The influence functional results from the Boltzmann weighted integration or trace over the N-m nonprimary states holding fixed the path- or time-dependent occupation of the primary states.

For the case in which m = 1, the analysis of this influence functional for the general class of N-state systems is isomorphic with that for a system of N+1 identical noninteracting fermions which evolve in a space of determinantal wave functions composed of N + 1 single particle states. In that isomorphic case, the influence functional determines the weight for the path function n(t). Here, n(t) is the occupation number for a particular single particle state in the imaginary time interval between 0 and iβ. As usual, β = 1/kT is Boltzmann’s constant times temperature, and 2πℏ is Planck's constant.

The derivation of the influence functional is given in Sec. II. The result is quite general, not dependent upon the particular division into N-m secondary states and m primary states. Of course, for any specific system, physical considerations may well dictate the particular partitioning one might adopt. In any case, the exact influence functional derived in Sec. II is a complicated object, highly nonlocal in time.

In Sec. III we consider a simplified approximate functional. For special cases we adjust the approximate influence functional variationally and obtain extremely accurate results. The simplified action functional may be useful in future applications. In making these applications it will be important to combine the model we present here with a Gaussian bath which describes the possible multitude of states associated with small amplitude fluctuations. This extension is discussed in Sec. IV.

II. PARTITIONING AND INFLUENCE FUNCTIONAL

Consider N states which we assume form a complete set of states for a multiparticle quantum system. A subset composed of m of these states will be of primary interest, and the remaining N-m states will be removed from our explicit consideration. We will regard the latter set of secondary states as a "bath" coupled to the primary states. If we proceeded with standard Schrödinger quantum mechanics, this reduction of states could be accomplished with projection operator methods, and the role of the removed bath states would appear implicitly through an effective Hamiltonian. In the ap-
proach taken herein, however, the effects of the secondary or bath states are described in terms of an influence functional which determines the statistical weight of quantum paths through the primary states. Only in the most abstract sense can the two approaches be regarded as equivalent. Indeed, it seems difficult to begin with the effective Hamiltonian deduced from the usual projection operator development of the resolvent operator and then derive the influence functional presented below in Eqs. (2.8)--(2.10).

A. General case

In the notation we adopt, \( |s\rangle \) and \( |j\rangle \) refer to the state vectors of primary and bath states, respectively. The matrix elements of the Hamiltonian are of three types: those coupling one primary state to another, \( \langle s|H|s'\rangle \); those coupling a primary state to a secondary state,

\[
\langle s|H|j\rangle = t_{sj} = t_{js}^\dagger,
\]

and those coupling two secondary states,

\[
\langle j|H|j'\rangle = \Theta_{jj'}.
\]

These matrix elements determine the amplitude for transitions between the various states.

Schematically, we may picture the Hamiltonian matrix as

\[
H = \begin{bmatrix}
        H_0 & t \\
      t^\dagger & B
    \end{bmatrix},
\]

where \( H_0 \) is the \( m \times m \) matrix with elements \( \langle s|H|s'\rangle \). The partition function or generating functional

\[
Q = \text{Tr} \exp(-\beta H)
\]

can be viewed as the sum over all cyclic paths in the space of \( N \) states during an imaginary time interval of length \( \beta \hbar \). We can characterize a path with the occupation numbers \( n_1^{(\alpha)} \), \( n_2^{(\alpha)} \), ..., \( n_N^{(\alpha)} \) where \( n_i^{(\alpha)} \) is 1 if the system is in state \( i \) during time slice \( \alpha \) and zero otherwise. Clearly, one and only one of the \( n_i^{(\alpha)} \) is unity at any given instant. The time slices in Euclidean time are each of duration

\[
e\hbar = \beta \hbar / P,
\]

hence, \( \alpha \) is an integer extending between 1 and \( P \). The condition of cyclic paths implies

\[
n_i^{(\alpha+1)} = n_i^{(\alpha)}.
\]

In all the formulas below, we anticipate the continuum limit, \( P \to \infty \).

Figure 1 illustrates a section of a typical quantum path which passes through primary states and secondary states. From time slice \( \alpha + 1 \) to \( \alpha + k + 1 \), the system moves among secondary states, having departed from primary state \( s \) at time slice \( \alpha \). The system returns to the primary states at time slice \( \alpha + k + 2 \) when it arrives at state \( s' \). The statistical weight for all path sections of this type can be expressed as a path sum:

\[
\sum_{j_1} \sum_{j_2} ... \sum_{j_{P-k-1}} \sum_{j_k} \sum_{j_{k+1}} \sum_{j_{k+2}} ...
\]

\[
\langle s|e^{-\beta \hbar \sum_{i=1}^N n_i^{(\alpha)}}|j\rangle \langle j|e^{-\beta \hbar \sum_{i=1}^N n_i^{(\alpha+1)}}|j_{k+1}\rangle ...
\]

\[
\langle j_{k+1}|e^{-\beta \hbar \sum_{i=1}^N n_i^{(\alpha+1)}}|j_{k+2}\rangle ...
\]

\[
\langle j_{P-k-1}|e^{-\beta \hbar \sum_{i=1}^N n_i^{(\alpha+1)}}|j_k\rangle
\]

\[
= \epsilon^k \sum_{j_k} \exp(-e\hbar B) t_{j_k} n_j^{(\alpha+1)},
\]

where the first equality follows from the smallness of \( \epsilon \), i.e.,

\[
\langle s|\exp(-e\hbar \sum_{i=1}^N n_i)|j\rangle = \epsilon \epsilon n_1^{(\alpha)} + O(\epsilon^2).
\]

One way of indicating that a path evolves among the secondary states during the interval between \( \alpha \) and \( \alpha + k + 2 \) is to state the value of the number

\[
\prod_{j_{k+1}} \left[ 1 - \sum_{i=1}^N n_i^{(\alpha+1)} \right],
\]

where the sum is over all primary states, and the product is over the time slices between \( \alpha \) and \( \alpha + k + 2 \). The number is 1 when the path is in the bath region during that time interval, and it is zero otherwise. This observation allows us to formally integrate out the bath of secondary states leaving only the occupation numbers for the primary states to be considered explicitly. In particular, with Eq. (2.6) together with this observation, we may write

\[
Q = \sum_{\{n_1^{(\alpha)}\}_{\alpha=1}}^{\{s_1^{(\alpha)}\}, \ldots, \{s_N^{(\alpha)}\}} \exp\left( S \left( \{n_1^{(\alpha)}\}_{\alpha=1} \right) \right),
\]

where the summation is over the set of all \( n_1^{(\alpha)} \) under the restriction that \( \Sigma \alpha n_1^{(\alpha)} \) is either 0 to 1, and where the action functional has two parts,

\[
S = S_p + S_f.
\]

Here, \( S_p \) refers to the action when paths evolve entirely within the primary state region, and \( S_f \) is the influence functional contribution from the bath states. The analysis of \( S_f \) follows standard methods of discretized path integrals. One finds

\[
S_p = -\epsilon \sum_{\alpha} \langle s|H|s\rangle \sum_{\alpha} n_1^{(\alpha)} n_1^{(\alpha+1)}
\]

\[
+ \sum_{\alpha, \beta} \ln(-\epsilon \langle s|H|s'\rangle) \sum_{\alpha} n_1^{(\alpha)} n_1^{(\alpha+1)},
\]

while the influence functional contribution is

\[
S_f = \ln(\text{Tr}_\beta e^{-\beta B}) \prod_{\alpha} \left[ 1 - \sum_{\alpha} n_1^{(\alpha)} \right]
\]

\[
+ \sum_{\alpha=0}^{P-2} \ln(e^2 t_\alpha \cdot [\exp(-e\hbar B) \cdot t_{\alpha+1}])
\]

\[
\times \prod_{\alpha=0}^{P-1} \sum_{\alpha} n_1^{(\alpha)} \prod_{\alpha} \left[ 1 - \sum_{\alpha} n_1^{(\alpha+1)} \right] n_1^{(\alpha+2)},
\]

\[
(2.10)
\]
where $\text{Tr}_B$ denotes the trace over the secondary states, and we have exploited the fact that since $n^{(a)}_i$ is 0 or 1, $n^{(a)}_i$ taken to any integer power is simply $n^{(a)}_i$. It should be understood that the sums over $s$ extend over all the $m$ primary states, and the sums and products over $\alpha$ go from 1 to $P$.

In studying these equations for $S_f$ and $S_p$, it is helpful to consider a few examples of different paths with various combinations and numbers of transitions into and out of the primary states. The products of occupation numbers serve as test functions which identify the particular types of path sections, and through the sums over time slices, every section of the path is examined with these test functions. The influence action $S_f$ arises from paths or sections of paths which leave the primary states. The first term exhibited in Eq. (2.10) is the contribution when the entire path evolves in the secondary states, and when that happens, $\exp(S_f)$ is simply the partition function for the bath of secondary states. The second term in Eq. (2.10) gives the weight for paths which are only partially in that bath. Notice that the interactions in Eq. (2.9) are pair interactions coupling occupation numbers of nearest neighbor time slices. The interactions in Eq. (2.10), however, are multipoint and nonlocal in time. Further, although $\exp(-\xi B)$ is positive semidefinite for real $\xi$, the form $\exp(-\xi B) t_i^{(a)}$, for $s \neq s'$ is not necessarily positive or even real. Hence, the nonlocal interactions in Eq. (2.10) may be complex. The complex interactions that can occur in both $S_f$ and $S_p$ will give rise to negative weights for certain quantum paths. This feature is a manifestation of phase interference in quantum theory.

B. Special case: one primary state

The special case in which there is only one primary state will be the focus of much of our attention in the remainder of this paper. Let $n^{(a)}_i$ denote the occupation number of that one state for the $c$th time slice. Then,

$$S_p = -\varepsilon \sum_{\alpha} n^{(\alpha)}_i n^{(a+1)} + 1, \quad \text{(2.11)}$$

where $\varepsilon$ is the expectation value of the energy in the primary state, and

$$S_f = \ln \left( \text{Tr}_B e^{-\beta B} \right) \prod_{\alpha} (1 - n^{(a)}_i)$$

$$+ \sum_{k=0}^{P-2} \ln \left[ e^{\varepsilon t} \exp (-\varepsilon k B) t_i^{(a)} \right] \prod_{\alpha} n^{(\alpha)}_i (1 - n^{(\alpha+1)}_i) (1 - n^{(a+1)}_i). \quad \text{(2.12)}$$

It is interesting to note that by multiplying out the product, effectively integrating by parts, the second term in Eq. (2.12) can be rewritten as

$$\ln(e^{\varepsilon t}) \sum_{\alpha} \left[ n^{(\alpha)}_i (1 - n^{(\alpha+1)}_i) + (1 - n^{(\alpha)}_i) n^{(a+1)}_i \right]$$

$$- \varepsilon \xi \sum_{k=2}^{P-2} \sum_{n=0}^{P-1} \sigma(k) \prod_{\alpha} (1 - n^{(\alpha+1)}_i) \prod_{\alpha} (1 - n^{(a+1)}_i)$$

$$- \varepsilon e^2 \sum_{k=2}^{P-2} \sum_{n=0}^{P-1} \sigma(k) \prod_{\alpha} (1 - n^{(\alpha+1)}_i), \quad \text{(2.13)}$$

where $\xi = \beta_0 B t_i^{(a)}$ with $t_0 = t_i^{(a)}$, and

$$\gamma = -\frac{\partial}{\partial \ln \beta} \ln \left[ t_{\alpha} \exp \left( -\beta B t_i^{(a)} \right) \right],$$

and finally

$$\sigma(k) = -\frac{\partial^2}{\partial (ek)^2} \ln \left[ t_{\alpha} \exp \left( -ek B t_i^{(a)} \right) \right].$$

The first two terms in Eq. (2.13) and $S_p$ have the form of the action for an asymmetric two-level system in an external field, and the third term is the action corresponding to a diagonal Hamiltonian. The last term has no simple corresponding model, however, the $\sigma(k)$ is like a two-point time correlation function for the bath states. It is interesting to note that $\sigma(k)$ satisfies the sum rule

$$\varepsilon \sum_{k=2}^{P-2} \sigma(k) = (\gamma/\beta) - \xi.$$ 

C. Isomorphism: $N-1$ fermions and $N$ single-particle states

The special case described above is isomorphic with the action functional that is obtained when considering a system of $N_f = N-1$ identical fermions with $N$ single-particle states, and one integrates out the occupation numbers for all but one of the single particle states. To demonstrate the isomorphism, let $m_i^{(a)}$ denote the occupation number of the $i$th single particle state during the $c$th time slice. These numbers are either 0 or 1, and the restriction of a fixed number of particles gives

$$\sum_{i=1}^{N} m_i^{(a)} = N - 1. \quad \text{(2.14)}$$

Equivalently, we can use

$1 - m_i^{(a)} = n_i^{(a)} \quad \text{(2.15)}$

to indicate the absence of a particle in the single particle state $i$ during the time slice $a$. When there is no particle in state $i$, we say there is a hole in state $i$, and $n_i = 1$; otherwise, $n_i$ is zero. Since the system has $N-1$ particles and $N$ single particle states, there is always one hole, i.e.,

$$\sum_{i=1}^{N} n_i^{(a)} = 1. \quad \text{(2.16)}$$

As we establish the isomorphism in the next few paragraphs, we will see that this condition is the same as that encountered earlier when considering the occupation of multiparticle states. There we stated the condition as requiring that one and only one $n_i^{(a)}$ is always unity at every time slice.

The evolution of the system can be conceived of in terms of the diffusion of the hole through the space of single particle states. The nature of this motion is determined by the Hamiltonian. Let $|m_1, m_2, ..., m_N\rangle$ stand for a state vector of the $(N-1)$ particle system. These correspond to antisymmetric (determinental) wave functions. With these states, we assume that the Hamiltonian has the diagonal matrix elements

$$\langle m_i, m_2, ..., | H | m_1, m_2, ... \rangle = \sum_j c_j m_i \quad \text{(2.17)}$$

and the off-diagonal elements

$$\langle m_1, m_2, \ldots | H | m'_1, m'_2, \ldots \rangle = T_{ij} \prod_{k=1}^{m_k} (-1)^m_k$$

(2.18)

if $m_i = 0$, $m_i' = 1$, $m_i' = 1$, $m_i = 0$, and $m_k = m_k'$ for all other $k$. All other matrix elements vanish. These rules coincide to the space of states with $N - 1$ particles and the Hamiltonian

$$H = \sum_{i=1}^{N} c_i a_i^\dagger a_i + \sum_{i<j=1}^{N} (T_{ij} a_i^\dagger a_j + T_{ji} a_j^\dagger a_i),$$

(2.19)

where $a_i^\dagger$ and $a_i$ are the creation and annihilation operators, respectively, for the $i$th single particle state. The quantity $T_{ij}$ gives the transition amplitude for a particle to hop between states $i$ and $j$.

Let us now adopt the following notation:

$$c = \sum_{i=2}^{N} c_i,$$

(2.20)

$$t = (T_{12}, -T_{13}, T_{14}, -T_{15}, \ldots),$$

(2.21)

and $B$ denotes the Hamiltonian matrix for the $N - 1$ states permissible when $m_i$ is restricted to unity. That is, $c$ is the expectation value of the energy when the hole is in single particle state 1, and $B$ is the Hamiltonian which controls the diffusion of the hole through the space of $N - 1$ single particle states 2, 3, $\ldots$, $N$. The full Hamiltonian then has the matrix form

$$H = \begin{bmatrix} c & t \\ t^\dagger & B \end{bmatrix},$$

(2.22)

where $t$ and $t^\dagger$ are $N - 1$ dimensional row and column vectors, respectively, and $B$ is an $(N - 1) \times (N - 1)$ matrix.

The correspondence with the special case analyzed earlier is now clear. We may integrate out the occupation number for all but that for state 1. The resulting action functional for $m_i^{(a)}$ is exactly that given by Eqs. (2.8), (2.11), and (2.12) with $n_1^{(a)} = 1$, $m_1^{(a)}$ corresponding to the hole occupation number for single particle state 1. Notice that since we restrict the number of particles to $N - 1$, there will be no fluctuations in the bath (i.e., the assembly of $N - 1$ single particle states, 2, 3, $\ldots$, $N$) for those time intervals over which $n_i^{(a)} = 1$. Only when $n_1^{(a)} = 0$ is there flexibility for transitions in the bath. These observations may be used to clarify the physical meaning of the three terms contributing to $S$ as given in Eqs. (2.11) and (2.12).

III. SIMPLIFIED APPROXIMATE INFLUENCE FUNCTIONAL

The influence functional in Eq. (2.10) is factored into two parts. The first, which is local in time, determines the weight assigned to paths that remain entirely outside the manifold of primary states. The second, more complicated part accounts for paths that jump between the secondary states and the primary states. Let us now consider the possibility of modeling this general influence functional, $S_f$, with a two-state picture in which one does not distinguish between the different secondary states. In other words, the assembly or bath of secondary states will be pictured as one effective state.

For this purpose, we define $1 - n_i^{(a)}$ as the occupation number for the entire manifold of these secondary states during the $a$th time slice. That is,

$$n_i^{(a)} = 1, \text{ when any } n_i^{(a)} = 1,$$

$$= 0, \text{ otherwise,}$$

or equivalently

$$n_i^{(a)} = \sum_i n_i^{(a)}.$$  \hspace{1cm} (3.1)

A two-state model for the influence functional action would then correspond to the approximation

$$S_f \approx \left[ \ln(q) \right] \prod_\alpha (1 - n_i^{(a)}) + ea \sum_\alpha n_i^{(a)} n_i^{(a+1)}$$

$$+ e \delta \sum_\alpha (1 - n_i^{(a)})(1 - n_i^{(a+1)})$$

$$+ \left[ \ln(eK) \right] \sum_\alpha \left[ n_i^{(a)}(1 - n_i^{(a+1)}) + (1 - n_i^{(a)}) n_i^{(a+1)} \right],$$

(3.2)

where $q$ is the partition function for the secondary "state" in the model, $a$ and $b$ are energy shifts associated with the primary and secondary states, respectively, and $K$ is the overlap or resonance integral of that effective secondary state with the manifold of primary states. The quantities $q$, $a$, $b$, and $K$ are the parameters with which we characterize the influence of a multitude of secondary states on the quantum paths of a few primary states.

Notice that the non-Gaussian nature of the approximate influence functional rests entirely with the first term in Eq. (3.2). The consequences of this term are relatively simple to analyze since it is nonzero for only one class of paths—those that remain entirely outside the primary states. The use of Eq. (3.2) combined with $S_f$ given in Eq. (2.9) yields a quantum mechanics problem equivalent to the diagonalization of an $(m + 1) \times (m + 1)$ Hamiltonian matrix. Thus, once the parameters $q$, $a$, $b$, and $K$ are identified, Eq. (3.2) affords a major simplification.

To test whether Eq. (3.2) is an accurate approximation, we have examined its behavior in an optimal variational sense for the special case of a single primary state coupled to $N - 1$ secondary states. This case is the one that is isomorphic with that of $N - 1$ fermions that can move among the configurations formed from $N$ single particle states. In general, the variational procedure is carried out along the following lines: Let

$$\Delta S = S_f - S_f,$$

(3.3)

Then the partition function can be expressed as

$$Q = Q_{\text{ref}} \left( \exp(\Delta S) \right)_{\text{ref}},$$

(3.4)

where $Q_{\text{ref}}$ and $\langle \ldots \rangle_{\text{ref}}$ indicate the partition function and ensemble average carried out with weight determined by the approximate influence action functional given in Eq. (3.2). Equation (3.4) is exact, but the average in the right-hand side is difficult to perform. However, the analysis of low order perturbation theory is usually computationally convenient.
Further, when $\Delta S$ is real, first order perturbation theory provides the following bound:

$$Q \geq \text{ref} \exp(\langle \Delta S \rangle_{\text{ref}}).$$

(3.5)

For the special case of a single primary state, it is easy to establish that $\Delta S$ is indeed real. This fact follows from noting that since $B$ is Hermitian, then $\exp(-i\beta H)$ is positive semidefinite. Hence, for this special case, we may adjust the parameters $q$, $a$, $b$, and $K$ so as to optimize the right-hand side of Eq. (3.5).

In practice, one might avoid the variational calculation and empirically determine $q$, $a$, $b$, and $K$. In principle, however, the variational calculation or other applications of perturbation theory provide a systematic basis for finding the best possible single state model for the manifold of secondary states. The results presented below indicate that when optimized, the model is extremely accurate.

We now consider explicitly the special case of a single primary state with $N - 1$ bath states. Equations (3.3), (3.2), (2.12), and the condition of cyclic boundary conditions yield

$$\Delta S = \ln[\text{Tr}_B \exp(-\beta H_B) + q \prod_{\alpha} (1 - n_{\alpha})]$$

$$-2\alpha \sum_{\alpha} n_{\alpha} \ln(1 - n_{\alpha} + 1) - \beta \sum_{\alpha} (1 - n_{\alpha}) (1 - n_{\alpha} + 1)$$

$$+ 2 \ln(|t|/K) \sum_{\alpha} n_{\alpha} (1 - n_{\alpha} + 1)$$

$$+ \sum_{k=0}^{P-1} \ln(t_k e^{-\beta e}) \sum_{\alpha=0}^{P-1} n_{\alpha}$$

$$\times \prod_{i=1}^{k+1} (1 - n_{\alpha} + \hat{n}_{\alpha} + k + 1).$$

(3.6)

The reference system average of all the last term in $\Delta S$ can be easily related to derivatives of the reference system partition function,

$$Q_{\text{ref}} = e^\epsilon(q - 1) + \cosh(\beta \lambda(0)/2),$$

(3.7a)

where

$$u = \beta (a + b)/2,$$

(3.7b)

$$v = \beta (b - a)/2,$$

(3.7c)

and

$$\beta \lambda(0)/2 = (u^2 - \beta^2 K^2)^{1/2}.$$

(3.7d)

The average of the last term in $\Delta S$ is more complicated. The result is

$$\langle \text{[last term in (3.6)]} \rangle_{\text{ref}}$$

$$= e^\epsilon(\beta K^2)/2Q_{\text{ref}} \left[ (1 - 2v/\beta \lambda(0)) \right.\right.$$

$$\times \int_0^1 dx \exp[(1 - x)\beta \lambda(0)/2 + xu] f(x)$$

$$+ (1 + 2v/\beta \lambda(0)) \int_0^1 dx \exp[-(1 - x)\beta \lambda(0)/2 + xu] f(x),$$

(3.8a)

where

$$f(x) = \ln(t_m e^{-\beta e} t_n).$$

(3.8b)

By adopting the notation

$$K = |t| e^{-2\alpha},$$

(3.9a)

and

$$\text{Tr}_B e^{-\beta H_B}/q = \exp(-bd),$$

(3.9b)

the variational equations are

$$D^2 \text{ln} Q_{\text{ref}} = \begin{bmatrix} \frac{\beta(a + c)}{\beta b} \\ \beta b \\ \beta d \end{bmatrix}$$

$$= D \text{[right-hand side of Eq. (3.8a)]},$$

(3.10)

where $D$ denotes the gradient operator with respect to the variational parameters $b\alpha, b\beta, \theta$, and $\beta d$.

With these equations, the approximate influence functional can be optimized. Representative results are shown in Table I for the Hamiltonian in Eq. (2.18) with $N = 5$,

$$e_{a - i} = 2 - i^2, \quad 1 < i < 5,$$

$$T_j = 0.1 \exp(-|c_i - c_j|) / \exp(-|c_i - c_j|) / \exp(-|c_i - c_j|), \quad j > i,$$

and

$$T_j = f \times (0.1) \times \exp(-|c_i - c_j|) / \exp(-|c_i - c_j|), \quad j > i.$$

State 1 is regarded as the primary state. The results of the approximate theory are compared with exact results, the latter found from straightforward matrix diagonalization.

Table I also shows results obtained by optimizing a fully Gaussian model for the influence functional. In particular,

<table>
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<th>$- \ln Q^+$</th>
<th>$1 - (n_i)^+$</th>
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<td>100</td>
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</table>

* Controls strength of coupling between primary and bath states.

* Helmholtz free energy.

* Average occupation number for primary state.
the non-Gaussian term in Eq. (3.2) was removed by setting \( q = 1 \), and a nonlocal term of the form

\begin{equation}
g \sum \alpha_n n^{(\alpha)} = g \left( \sum \alpha_n \right)^2 \tag{3.11}
\end{equation}

was added in its place. The partition function and correlation function for this reference system can be analyzed by introducing a one-dimensional Gaussian integration which uncompresses the square in the action functional of Eq. (3.11). The parameters \( g, a, b, \) and \( K \) were then optimized variationally. Except for very special instances where \( \langle n^{(\alpha)} \rangle_{\text{ref}} \) is exactly 1/2, the optimization finds \( g \) to be 0, and the fully Gaussian influence functional yields significantly inferior results to those found with the non-Gaussian (3.2).

IV. COUPLING TO A BOSONIC BATH

We now consider the situation where the \( N \)-state system is coupled to an environment. The latter is modeled as a Gaussian fluctuating medium—a bosonic bath. To be precise, the Hamiltonian is

\begin{equation}
\mathcal{H} = \mathcal{H}_0 + \frac{1}{\hbar} \sum_{j, i} \sum_{j, \delta} M_j \left( P_j + \omega_j X_j \right) + \sum_{j, i} \sum_{j, \delta} c_{ij} \langle i | j \rangle \langle j | i \rangle, \tag{4.1}
\end{equation}

where \( X_j \) is the \( j \)-th mode of the bosonic bath, \( M_j \), \( P_j \) is the conjugate momentum of \( X_j \), and \( \omega_j \) is its fundamental frequency. The constants \( c_{ij} \) specify the coupling of the harmonic modes to the \( N \) states, and \( \mathcal{H}_0 \) is the Hamiltonian of the \( N \) states in the absence of such coupling.

When the unperturbed system has only two states, i.e., \( N = 2 \), Eq. (4.1) is then the often studied “spin-boson” Hamiltonian.\(^ {10} \) It is used as a simplified model for describing the effects of a fluctuating environment on tunneling and charge transfer. Recent work has provided a number of useful methods for treating the spin-boson Hamiltonian, and perhaps the most accurate of these is the effective adiabatic (EA) approximation.\(^ {11} \) The basic idea in this approach is to determine variationally the adiabatic (zero frequency) bath which best mimics the effects of the dynamical bosonic bath. The resulting quantum mechanics to be performed in this approximation is merely more difficult than the diagonalization of \( \mathcal{H}_0 \)—a particularly simple task when \( N = 2 \).

Armed with this general procedure of the EA approximation, we can now address the question of how the reduction of \( N \) molecular states to a few primary states is affected by the presence of a fluctuating environment. The first step is to write down the action functional belonging to Eq. (4.1) after the bosonic bath has been integrated out. The path integrals for the bosonic bath are, of course, Gaussian integrals, and their evaluation results in

\begin{equation}
S = S_0 + \frac{1}{2P^2} \sum_{\alpha=1}^{N} \sum_{\alpha'=1}^{P} \sum_{\alpha''=1}^{P} n^{(\alpha)} z_{\alpha'} z_{\alpha''} |\alpha - \gamma| |\gamma|^{n^{(\alpha)}} \tag{4.2}
\end{equation}

where \( S_0 \) is the action functional for \( N \) states given in Eqs. (2.8)-(2.10), and

\begin{equation}
z_{\alpha}(\tau/\beta \hbar) = \langle y_\alpha(0) y_\alpha(\tau) \rangle, \quad 0 < \tau < \beta \hbar \tag{4.3}
\end{equation}

with

\begin{equation}
y_\alpha \equiv \sum_{j=1}^{L} c_{\alpha j} X_j, \tag{4.4}
\end{equation}

and the notation \( \langle ... \rangle_\beta \) indicates that the correlation function is evaluated for the pure harmonic bath. One has

\begin{equation}
z_{\alpha}(\tau/\beta \hbar) = \sum_{\beta} c_{\alpha \beta} \langle x_\alpha(0) x_\beta(\tau) \rangle
= \sum_{\beta} c_{\alpha \beta} [ M_\beta \omega_\beta^2 \beta \sinh(\beta \hbar \omega_\beta/2) ]^{-1}
\times \cosh(1/\hbar \omega_\beta) \cdot \beta \hbar \omega_\beta. \tag{4.5}
\end{equation}

In the EA procedure, we construct a reference action functional belonging to an adiabatic or zero frequency bath Hamiltonian. In other words, the second term in Eq. (4.2) is replaced by

\begin{equation}
(1/2P^2 \sum_{\alpha=1}^{N} \sum_{\alpha'=1}^{P} n^{(\alpha)} z_{\alpha'} z_{\alpha''} |\alpha - \gamma| |\gamma|^{n^{(\alpha)}} \tag{4.6}
\end{equation}

where \( z_{\alpha} \) are adjustable time independent parameters corresponding to the variance of the zero frequency fluctuating fields of the fictitious adiabatic bath. Further, in the EA reference system, one considers replacing \( S_0 \) by \( S_\beta \) where the prime indicates that the parameters characterizing the uncoupled Hamiltonian can be adjusted too. The adjustments are made within the context of low order perturbation theory. In particular, if \( S_0 \) is real, then the parameters can be determined by optimizing the bound of first order perturbation theory. Otherwise, one may adjust the parameters to make first order terms equal to zero.

In the previous section we have brought these procedures one step beyond the EA method by introducing an approximate \( S_{\text{ref}} \). Combining this simplification with the EA approach suggests the following reference action functional

\begin{equation}
S_{\text{ref}} = S_\beta + S_\gamma \text{ [in Eq. (3.2); } q, a, b, K \text{ ]}
+ (1/2P^2 \sum_{\alpha=1}^{N} \sum_{\alpha'=1}^{P} n^{(\alpha)} z_{\alpha'} z_{\alpha''} |\alpha - \gamma| |\gamma|^{n^{(\alpha)}} \tag{4.6}
\end{equation}

where all the primed quantities along with \( q, a, b, \) and \( K \) are adjustable parameters.

We have tested the utility of this model by considering the case in which there is only one primary state, and it is that state which is coupled to the environmental bath. It is the latter circumstance—only the primary states are coupled to the environment—for which the approach dictated by Eq. (4.6) should be particularly useful. As noted in Sec. III, the action is real when there is only one primary state. Hence, for this special case, the variational procedure can be used to optimize the reference system. Therefore, we write

\begin{equation}
S_{\text{ref}} = - g \sum_{\alpha=1}^{N} n^{(\alpha)} n^{(\alpha)} + S_\gamma \text{ [in Eq. (3.2)]}
+ (z^2/2 \left[ \frac{1}{P} \sum_{\alpha=1}^{N} n^{(\alpha)} \right]^2. \tag{4.7}
\end{equation}

The difference between \( S_{\text{ref}} \) and the full action for this problem is

\begin{equation}
\Delta S = S_\gamma \text{ [in Eq. (2.12)]} - S_\gamma \text{ [in Eq. (3.2)]}
+ (1/2P^2 \sum_{\alpha=1}^{N} \sum_{\alpha'=1}^{P} n^{(\alpha)} z_{\alpha'} z_{\alpha''} |\alpha - \gamma| |\gamma|^{n^{(\alpha)}}. \tag{4.8}
\end{equation}
### TABLE II. Occupation numbers for a primary state and solvation chemical potentials for a five-state model system coupled with strength $\varepsilon'$ to a monochromatic harmonic bath with frequency $\omega$.\(^6\)

<table>
<thead>
<tr>
<th>$f$</th>
<th>1 - $\langle n_i \rangle$</th>
<th>$\tilde{\beta}_i \mu^i$</th>
<th>$f \varepsilon = \beta \hbar \omega = 2$</th>
<th>1 - $\langle n_i \rangle$</th>
<th>$\tilde{\beta}_i \mu^i$</th>
<th>$f \varepsilon = \beta \hbar \omega = 10$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.726</td>
<td>0.263</td>
<td>-1.0129</td>
<td>0.496</td>
<td>0.118</td>
<td>-1.499</td>
</tr>
<tr>
<td>1</td>
<td>0.724</td>
<td>0.264</td>
<td>-1.012</td>
<td>0.496</td>
<td>0.119</td>
<td>-1.4355</td>
</tr>
<tr>
<td>10</td>
<td>0.633</td>
<td>0.290</td>
<td>-0.9516</td>
<td>0.497</td>
<td>0.207</td>
<td>-1.1573</td>
</tr>
<tr>
<td>100</td>
<td>0.500</td>
<td>0.463</td>
<td>-0.5809</td>
<td>0.500</td>
<td>0.463</td>
<td>-0.5810</td>
</tr>
<tr>
<td>0.1</td>
<td>0.0000012</td>
<td>-8.7071</td>
<td></td>
<td>0.00005</td>
<td>-9.3149</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.000022</td>
<td>-8.7027</td>
<td></td>
<td>0.00015</td>
<td>-9.3058</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0.0000006</td>
<td>-8.3152</td>
<td></td>
<td>0.000099</td>
<td>-8.6319</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>0.030100</td>
<td>-4.2003</td>
<td></td>
<td>0.030095</td>
<td>-4.2011</td>
<td></td>
</tr>
</tbody>
</table>

\(^6\)The parameter $\varepsilon$ is the classical solvation energy as defined in Ref. 11. In terms of the notation in this paper, $\beta \varepsilon$ is $[c_1]$.\(^7\)

Then the first order perturbation theory bound is once again $Q_i \geq Q_{i,ref} \exp(\Delta S_{i,ref})$. All five parameters $q, a, b, K$, and $\varepsilon'$ are varied simultaneously to optimize this bound. Implementation of this procedure requires the derivations of the formulas already sketched in Sec. III and Ref. 11. Therefore, details are omitted in the sake of brevity. The variational equations lead to an algebraic fixed point problem which was solved by the Picard method and the singular value decomposition of the corresponding set of linear equations.\(^2\)

Table II presents representative results we have obtained for the five-state model described in Sec. III when it is coupled to a monochromatic bath (i.e., an Einstein crystal). We compare our results with those obtained with a pure two-level system neglecting all but the first two terms in the exact influence function, $S_f$, as given in Eq. (2.13). The comparison shows that the simple two-state model without non-Gaussian terms is accurate when the bath stabilizes the primary state to such an extent that the secondary states are rarely visited. It is also accurate for unusually large interstate couplings which smear the distinction between the secondary states. Otherwise, the non-Gaussian term we have introduced in Eq. (3.2) plays an important role, one which may have significant implications in a variety of applications in which one requires a reduced model of many electron molecules.

The utility of the model we have suggested will depend on its transferability from one situation to another. To examine the possibility of transferability, we have performed the following calculation: (1) The simplified influence functional in Eq. (3.2) was optimized in the absence of the bosonic bath (i.e., the parameters $q, a, b, K$, and $\varepsilon'$ were determined as in Sec. III). (2) The bosonic bath was then coupled to the reduced model and the solvation by the bath was analyzed with the EA procedure. We will call this two-step calculation "Procedure A" and contrast it with the full simultaneous optimization of all the parameters. The latter calculation, already discussed in Table II, we will call "Procedure B." In Table III we show a representative comparison of the two procedures. The results of the two methods are nearly identical, indicating that with a judicious choice of primary states (those which couple strongly to the environment), the reduction of a complicated multistate molecular system to a simplified few-state model can be performed before one considers the effects of small amplitude fluctuations or various environments on the molecular system.

### V. SUMMARY

We have presented in Eq. (2.10) the exact action influence functional that results from integrating out $N-m$ secondary many electron states leaving only $m$ primary states for explicit consideration. With Eq. (3.2), we propose a simplified approximate influence functional corresponding to a

### TABLE III. Two procedures for calculating the effects of solvation of five-state system.\(^8\)

<table>
<thead>
<tr>
<th>$\beta \varepsilon = \beta \hbar \omega$</th>
<th>1 - $\langle n_i \rangle$</th>
<th>$\beta \mu^i$</th>
<th>1 - $\langle n_i \rangle$</th>
<th>$\beta \mu^i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Procedure A</td>
<td>Procedure B</td>
<td>Procedure A</td>
<td>Procedure B</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.29014</td>
<td>0.290136</td>
<td>-0.95158</td>
<td>0.95161</td>
</tr>
<tr>
<td>10</td>
<td>0.01005</td>
<td>0.01006</td>
<td>-8.31532</td>
<td>-8.31524</td>
</tr>
</tbody>
</table>

\(^8\)The five-state system is the same as that considered in Tables I and II with $f = 10$. Procedures A and B are defined in the text. All symbols are the same as those defined for Tables I and II.
model in which the bath of secondary states is replaced by a single effective state. For specific examples, we have shown that the simplified functional can be extremely accurate. In practice, it will probably be most useful to identify the parameters characterizing the simplified model by empirical methods rather than by optimization calculations of the type carried out herein. Fortunately, the last set of calculations presented above suggest that the empirical model parameters will have a significant degree of transferability from one system to another.

As a final remark, we call attention to the fact that except for the single non-Gaussian term which contributes to only one path in the sum of paths through primary states, the approximate influence action functional is local in time. The original action functional, the one appropriate to the entire space of states, is also local in time with interactions of the same form as those in the approximate influence functional. Thus, within the context of our approximate influence functional, the action functional for the reduced set of states has virtually the same form as that for the full set. This observation suggests the possibility of useful renormalization group developments of small basis set descriptions of many electron systems.


For example, when \( \Delta S \) is complex, the variational principle does not apply. However, it is always possible to adjust the coefficients characterizing the reference system so that the first order perturbation theory contributions for various quantities vanish.

