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Perturbation theory for nonlinear time-independent Schrödinger equations

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A special nondegenerate perturbation theory is developed for solving the "nonlinear Schrödinger equation" of the type $[\hat{H}+\hat{V}(\Psi)]\Psi=E\Psi$, which arises, e.g., from the study of the environmental effects on molecules. The interaction operator is taken as $\hat{V}(\Psi)=\hat{A}\langle\Psi|\hat{B}|\Psi\rangle$. The *in vacuo* problem $\hat{H}\Phi=\epsilon\Phi$ is considered the zeroth-order description. For the perturbed energies and wave functions recursive formulas are derived at any order of the perturbation. The formulas obtained are compared to the usual Rayleigh-Schrödinger perturbation theory where $\hat{V}$ is supposed to be independent of Ψ. The formal results are applied to the case of the Onsager cavity model.

I. INTRODUCTION

Physical systems are usually treated *in vacuo,* i.e., by supposing that they are not affected by their surroundings. This fictious model often works well but there are many important cases where the interaction with the environment is to be taken into account explicitly. For example, most quantum-chemical calculations are performed within the isolated-molecule approach where the goal is generally to solve the time-independent Schrödinger equation

$$\hat{H}\Phi_i=\epsilon_i\Phi_i \ . \tag{1}$$

In Eq. (1) $\hat{H}$ is the Hamiltonian of the isolated molecule. However, in studying chemical problems it is often necessary to consider environmental effects on the molecule under study.[1] The interaction between the system and its environment is usually taken into account by introducing an effective potential $\hat{V}$ into the Hamiltonian. The environment itself is not treated explicitly. The determination of the actual form of $\hat{V}$ presupposes the specification of some physical model. A particularly interesting situation is when the environment is not taken to be "rigid," that is, the effect of the molecule on the environment is also considered. In this case, the interaction potential $\hat{V}$ will depend on the wave function of the molecule itself and one gets the following type of nonlinear Schrödinger equation[2–4]:

$$[\hat{H}+\hat{V}(\Psi_i)]\Psi_i=E_i\Psi_i \ . \tag{2}$$

Usually we can assume that the interaction potential $\hat{V}$ depends on Ψ_i through the expectation value of an operator.[2–10] This assumption permits us to write Eq. (2) in form

$$(\hat{H}+\lambda\hat{A}\langle\Psi_i|\hat{B}|\Psi_i\rangle)\Psi_i=E_i\Psi_i \ , \tag{3}$$

where $\hat{A}$ and $\hat{B}$ are operators depending on the particular choice for the interaction model, while λ is a parameter characterizing the strength of interaction. Note that E_i, in Eqs. (2) and (3), is the effective energy of the system (molecule) containing the *in vacuo* energy ϵ_i and the total interaction with the environment.

One physical example leading to such an equation is the problem of a molecule in a polarizable medium, treated by the classical Kirkwood[11] and Onsager[12] interaction models. For example, in the simple dipole approximation both operators $\hat{A}$ and $\hat{B}$ correspond to the dipole-moment operator of the molecule, while λ depends on the mean static dielectric constant of the environment.[2,5,7]

It is apparent that Eq. (3) can be solved iteratively for a given state i. It should be noted that Eq. (3) cannot be deduced from the variational principle applied to the usual energy functional $\langle\Psi|\hat{H}'|\Psi\rangle/\langle\Psi|\Psi\rangle$; an appropriate variational functional was proposed by Sanhueza *et al.*[13]

Application of the standard Rayleigh-Schrödinger (RS) perturbational theory, or the use of some variational methods, e.g., the configuration-interaction (CI) procedure, involves the evaluation of the off-diagonal elements of the Hamiltonian $\langle\Phi_i|\hat{H}'|\Phi_k\rangle$ over approximate wave functions Φ_i. These procedures cannot be applied in a straightforward manner to solve nonlinear equations of type (3), because in handling the off-diagonal elements, some ambiguity arises as a consequence of the state dependency in the Hamiltonian $\hat{H}'(\Psi_i)$

$$\hat{H}'(\Psi_i)=\hat{H}+\lambda\hat{A}\langle\Psi_i|\hat{B}|\Psi_i\rangle \ . \tag{4}$$

Therefore, in this paper we develop a special type of nondegenerate perturbational theory (PT) for solving Eq. (3), where the state dependence of $\hat{H}'(\Psi_i)$ is treated explicitly. The molecular problem *in vacuo* is supposed to be solved. This solution is considered as the zeroth-order description, while the interaction operator $\lambda\langle\Psi_i|\hat{B}|\Psi_i\rangle\hat{A}$ represents the perturbation. The strength of the coupling is characterized by λ which can be considered as a perturbation parameter.

We should like to point out that the problem of the nonlinear Schrödinger equation of type (3) is rather general; the treatment of the interaction of a molecule and its environment represents a special application, which will be discussed in Sec. VI.

II. PERTURBATION OF THE WAVE FUNCTION

Let us expand the exact wave function Ψ_i in a perturbational series characterized by the perturbation parameter λ, in terms of the zeroth-order solutions Φ_j:

$$\Psi_i=\Phi_i+\sum_{\mu=1}^{\infty}\lambda^{\mu}\sum_{j\,(\neq i)}C_{ij}^{\mu}\Phi_j\ , \tag{5}$$

where μ labels the order of the perturbation and $C_{ij}^{(\mu)}$ is the expansion coefficient of Ψ_i on Φ_j $(j\neq i)$. Note that the spectrum of $\hat{H}$ is supposed to be discrete and the so-called intermediate normalization condition is used

$$\langle\Psi_i\,|\,\Phi_i\rangle=1\ .$$

The perturbation series for the eigenvalues E_i is written in a similar form

$$E_i=\epsilon_i+\sum_{\mu=1}^{\infty}\lambda^{\mu}E_i^{(\mu)}\ . \tag{6}$$

Our aim is to derive expressions for $C_{ij}^{(\mu)}$ and $E_i^{(\mu)}$.

III. LOW-ORDER CONTRIBUTIONS

Let us substitute Eqs. (5) and (6) into the nonlinear Schrödinger equation (3). In the zeroth order, collecting the terms independent of λ, we recover Eq. (1) as expected. The terms linear in λ give

$$\hat{A}\langle\Phi_i\,|\,\hat{B}\,|\,\Phi_i\rangle\Phi_i+\hat{H}\sum_{j\,(\neq i)}C_{ij}^{(1)}\Phi_j=E_i^{(1)}\Phi_i+\epsilon_i\sum_{j\,(\neq i)}C_{ij}^{(1)}\Phi_j\ . \tag{7}$$

Utilizing Eq. (1), and taking the scalar product of (7) with Φ_i, we obtain

$$E_i^{(1)}=A_{ii}B_{ii}\ , \tag{8}$$

where we introduced the matrix-element notation

$$A_{ik}=\langle\Phi_i\,|\,\hat{A}\,|\,\Phi_k\rangle\ .$$

The scalar product of Eq. (7) with Φ_k $(k\neq i)$ gives

$$C_{ik}^{(1)}=\frac{A_{ki}B_{ii}}{\epsilon_i-\epsilon_k}\ . \tag{9}$$

Note again that the zeroth-order states are assumed to be nondegenerate.

Equations (8) and (9) represent the solutions at the first order of perturbation theory (PT). These formulas show that, if we identify the perturbation operator $\hat{V}$ with $B_{ii}\hat{A}$, a result equivalent to that of the standard Rayleigh-Schrödinger PT is obtained. [This identification is straightforward since $B_{ii}\hat{A}$ represents that part of the Hamiltonian (4) which is linear in λ.] In other words, the nonlinearity of Eq. (3) has no special effect at the first order. This is quite natural since, from the perturbational point of view, the nonlinearity of Eq. (3) arises from the fact that the Hamiltonian (4) also contains operators proportional to λ^2, λ^3, etc., but these terms do not enter at the first order.

For determining the second-order formulas we have to pick up terms depending on λ^2. The results are

$$E_i^{(2)}=\sum_k{}'\frac{A_{ki}B_{ii}}{\epsilon_i-\epsilon_k}(A_{ik}B_{ii}+2A_{ii}B_{ik}) \tag{10}$$

and

$$C_{ij}^{(2)}=\sum_k{}'\frac{A_{ki}B_{ii}}{(\epsilon_i-\epsilon_k)(\epsilon_i-\epsilon_j)}(A_{jk}B_{ii}+2A_{ji}B_{ki})-\frac{A_{ii}A_{ji}B_{ii}^2}{(\epsilon_i-\epsilon_j)^2}\ , \tag{11}$$

where the prime on the summation means the restriction $k\neq i$.

Comparing these results with those of the standard RS PT, we can see that some new terms occur at the second order due to the nonlinearity of Eq. (3). In $E_i^{(2)}$, this "nonlinearity term" is $2A_{ii}B_{ii}\sum'_{(k)}A_{ik}B_{ik}/(\epsilon_i-\epsilon_k)$ while $C_{ij}^{(2)}$ can be written as

$$C_{ij}^{(2)}=C_{ij}^{(2)}(\text{RS})+2\frac{A_{ji}B_{ii}}{\epsilon_i-\epsilon_j}\sum_k{}'\frac{A_{ki}B_{ki}}{\epsilon_i-\epsilon_k}\ , \tag{12}$$

where $C_{ij}^{(2)}(\text{RS})$ is the corresponding Rayleigh-Schrödinger result. Generally, it is not surprising that the nonlinearity terms are those which contain off-diagonal B_{ik} matrix elements.

We give the third-order energy expression which reads

$$E_i^{(3)}=B_{ii}\sum_k{}'C_{ik}^{(2)}A_{ik}+2A_{ii}\sum_k{}'C_{ik}^{(2)}B_{ik}+2\sum_{k,l}{}'C_{ik}^{(2)}C_{il}^{(1)}A_{il}B_{ik}+A_{ii}\sum_{k,l}{}'C_{ik}^{(1)}C_{il}^{(1)}B_{kl} \tag{13}$$

with $C^{(1)}$ and $C^{(2)}$ defined above. Here, using again the indentification $\hat{V}=B_{ii}\hat{A}$ suggested by the first-order results, the RS contribution is that in the first sum, while further terms arise from the nonlinearity.

IV. RECURSION FORMULAS FOR ARBITRARY ORDER μ

One can derive recursion relations for $C_{ij}^{(\mu)}$ and $E_i^{(\mu)}$ at the general order μ. Substituting Eqs. (5) and (6) into Eq. (3), picking up the terms which are of order μ in λ and utilizing Eq. (1) one obtains

$$\begin{aligned}E_i^{(\mu)}=&\sum_k{}'C_{ik}^{(\mu-1)}A_{ik}B_{ii}\\&+2A_{ii}\sum_k{}'C_{ik}^{(\mu-1)}B_{ik}\\&+\sum_{\nu=1}^{\mu-2}\sum_{kl}{}'C_{ik}^{(\nu)}C_{il}^{(\mu-\nu-1)}(A_{il}B_{kl}+2A_{il}B_{ik})\\&+\sum_{\substack{\nu,\tau\\(\nu+\tau<\mu-2)}}\sum_{klm}{}'C_{ik}^{(\nu)}C_{il}^{(\tau)}C_{im}^{(\mu-\nu-\tau-1)}A_{im}B_{kl}\end{aligned} \tag{14}$$

and

$$\begin{aligned}C_{ij}^{(\mu)}=&B_{ii}\sum_k{}'C_{ik}^{(\mu-1)}A_{jk}/(\epsilon_i-\epsilon_j)-\sum_{\nu=1}^{\mu-1}\frac{E_i^{(\nu)}C_{ij}^{(\mu-\nu)}}{\epsilon_i-\epsilon_j}+2\sum_k{}'C_{ik}^{(\mu-1)}A_{ji}B_{ki}/(\epsilon_i-\epsilon_j)\\&+\sum_{\nu=1}^{\mu-2}\sum_{k,l}{}'C_{ik}^{(\nu)}C_{il}^{(\mu-\nu-1)}\frac{A_{ji}B_{kl}+2A_{jl}B_{ki}}{\epsilon_i-\epsilon_j}+\sum_{\substack{\nu,\tau\\(\nu+\tau<\mu-2)}}\sum_{k,l,m}{}'C_{ik}^{(\nu)}C_{il}^{(\tau)}C_{im}^{(\mu-\nu-\tau-1)}A_{jm}B_{kl}/(\epsilon_i-\epsilon_j)\ .\end{aligned} \tag{15}$$

These formulas are valid for $\mu \geq 4$. Terms containing triple summations over k, l, and m are to be omitted to obtain the third-order expressions. Second-order results can be recognized by dropping the terms with double summations over k and l as well.

The recursion formulas (14) and (15) contain contributions from all previous orders. As to the eigenvalues this is a typical nonlinearity effect, since in the RS PT one has the simple recursion relation

$$E_i^{(\mu)} = \sum_k{}' C_{ik}^{(\mu-1)} V_{ik} ,$$

where V_{ik} represents the matrix element of the perturbation operator. Thus, terms in the second, third, and fourth lines of Eq. (14) originate from the nonlinearity of the Hamiltonian, or in other words, from the influence of the system on its environment.

As for the expansion coefficients, the standard RS PT yields to the following recursion relation:

$$C_{ij}^{(\mu)}(\mathrm{RS}) = \frac{\sum_k{}' C_{ik}^{(\mu-1)} V_{jk} - \sum_\nu E_i^{(\nu)} C_{ij}^{(\mu-\nu)}}{\epsilon_i - \epsilon_j} ,$$

which can be put into analogy with the first two sums of Eq. (15). Any other terms represent nonlinearity effects.

Investigation of the general convergence properties of the perturbational expansions (5) and (6) for the nonlinear equation (4) seems to be rather cumbersome. Formal convergence criteria, available for general perturbations (see the contribution by Palmer in Ref. 14), are not applicable in the present case due to the wave-function dependency of the perturbation operator $\hat{V}$. However, since Eqs. (5) and (6) are *power series* in λ they will converge (for $|\lambda| < 1$) provided that the coefficients ($E_i^{(\mu)}$ and $\sum'_{(k)} C_{ik}^{(\mu)} \Phi_k$) are bounded. We note that in the treatment of environmental effects this formal condition is generally fulfilled (see also Sec. VI). Special attention should be paid to the particular case, when the spectrum of the zeroth-order Hamiltonian is quasidegenerate, because of the expected divergence of the pertubational expansions.

V. COMPARISON WITH RELATED PROBLEMS

The development of the perturbational scheme proposed in this paper was stimulated by the problem of quantum-chemical treatment of a molecule in a polarizable medium. However, the general form of the perturbation operator $\hat{A}\langle \Psi | \hat{B} | \Psi \rangle$ permits us to use the above results for a rather widespread class of interacting quantum systems. It should be noted that although there exist some related problems where the quantum system is described by nonlinear equations, due to the differences in the form of the nonlinear terms, the presented scheme cannot be applied without further changes. Such problems are, e.g., the solution of the time-dependent nonlinear Schrödinger equation (see Ref. 15 and references therein), or the "self-consistent—field perturbation theory"[16,17] at the Hartree-Fock level. In the latter case, the problem of nonlinearity arises from the need of a self-consistent field describing electron-electron interactions in the Hartree-Fock model. In spite of certain similarities, our approach is not equivalent to the self-consistent—field (SCF) perturbation theory since the Hartree-Fock operator cannot be written in the form of Eq. (4).

VI. APPLICATION: THE ONSAGER CAVITY MODEL

In this section we apply our formal results to the special example of a molecule interacting with its solvent environment. The Onsager reaction field (spherical cavity) model,[12] which is widely used in quantum-chemical calculations to account for environmental effects[2,5,7] leads to the following form of the nonlinear perturbation in Eq. (2) (Ref. 2):

$$\hat{V}(\Psi) = -\frac{1}{a^3}\frac{2(\epsilon-1)}{2\epsilon+1}\hat{M}\langle \Psi | \hat{M} | \Psi \rangle , \tag{16}$$

where $\hat{M}$ is the dipole-moment operator, a is the radius of the cavity, and ϵ is the static dielectric constant of the solvent. We choose a dimensionless perturbation parameter λ as

$$\lambda = \frac{2(\epsilon-1)}{2\epsilon+1}\frac{a_0^3}{a^3} \tag{17}$$

(a_0 is the Bohr radius) to represent the strength of the coupling between the molecule and its environment. In any real situation $\lambda < 1$, since $a > a_0$ and $2(\epsilon-1)/(2\epsilon+1) \leq 1$.

The comparison with Eq. (4) shows that we can identify the operators $\hat{A}$ and $\hat{B}$ with

$$\hat{A} = -\hat{M} , \tag{18a}$$

$$\hat{B} = \hat{M}/a_0^3 . \tag{18b}$$

Using atomic units we set $a_0 = 1$ in the following.

Substitution of Eqs. (17) and (18) into the general energy correction formulas yields

$$E_i^{(1)} = -M_{ii}^2 , \tag{19}$$

$$E_i^{(2)} = -3M_{ii}^2 \sum_k{}' \frac{M_{ik}^2}{\epsilon_k - \epsilon_i} , \tag{20}$$

$$E_i^{(3)} = 3M_{ii}^4 \sum_k{}' \frac{M_{ik}^2}{(\epsilon_k - \epsilon_i)^2} - 4M_{ii}^2 \sum_{k,l}{}' \frac{M_{ik} M_{il}}{(\epsilon_k - \epsilon_i)(\epsilon_l - \epsilon_i)} (M_{ii} M_{il} + 2M_{ik} M_{il}) . \tag{21}$$

Introducing the total dipole moment $\mu_i = M_{ii}$ and the polarizability α_i of the molecule as

$$\alpha_i = 2\sum_k{}' \frac{M_{ik}^2}{\epsilon_k - \epsilon_i} , \tag{22}$$

we can gain some insight into the physical meaning of corrections (19) and (20).

The total effective energy $E_i = \epsilon_i + \sum_{\mu=1}^{\infty} \lambda^\mu E_i^{(\mu)}$ reads

$$E_i = \epsilon_i - \mu_i R_i - \tfrac{3}{2}\alpha_i R_i^2 + \mathcal{O}(\lambda^3) , \tag{23}$$

where the reaction field R_i is defined[18] as

$$R_i = \frac{1}{a^3}\frac{2(\epsilon-1)}{2\epsilon+1}\mu_i . \tag{24}$$

As we have mentioned in Sec. I, E_i contains the total interaction energy between the molecule and its surroundings. Let us define the "self energy" of the molecule as

$$E_i=\epsilon_i+\tfrac{1}{2}\sum_{\mu=1}^{\infty}\lambda^{\mu}E_i^{(\mu)}\ , \tag{25}$$

where the introduction of the factor $\frac{1}{2}$ corresponds to subtracting the energy spent by the molecule to polarize its environment.[18] Then we essentially recover the familiar formula for the electrostatic free energy of solvation[18]

$$E_i=\epsilon_i-\tfrac{1}{2}\mu_i R_i-\tfrac{3}{4}\alpha_i R_i^2+\cdots\ . \tag{26}$$

The first term on the right-hand side of Eq. (26), ϵ_i is the energy of the isolated molecule. The second term represents the energy of a rigid point dipole immersed into a polarizable medium (classical reaction field energy), while the last term of order two describes the interaction of the induced dipole moment of the molecule with the reaction field of the permanent dipole moment μ_i. This latter effect accounts for the response of the molecule to the influence of the polarized environment. Higher-order energy corrections derived in this paper [see, e.g., Eq. (21)] take into account changes in the reaction field itself.

The pertubational approach proposed here permits us to obtain the interaction energy (and the perturbed wave functions also) in terms of the solutions for the isolated molecule. This approach appears to be simpler than the iterative methods leading to self-consistent reaction fields, and allows us to treat both the ground and excited states on an equal footing.

The proposed theory, in principle, can also be applied for the case of coupling schemes other than the Onsager cavity model (e.g., continuum[2–9] and discrete[10] models).

Interactions arising between a molecule and its surroundings are intermolecular in nature, so they are at least of an order of magnitude smaller than intramolecular interactions involved in the zeroth-order Hamiltonian. Accordingly, the strength of the perturbation will be relatively small and it is reasonable to expect that the perturbational series will converge fast in almost all practical (nondegenerate) situations. The effectivity of the method remains to be tested by numerical applications.

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