NONLINEAR SCHRÖDINGER EQUATIONS AND INTERMOLECULAR INTERACTIONS

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Abstract

Nonlinear time-independent Schrödinger equations arise if the model Hamiltonian depends on the wave function. This may occur if certain interactions are accounted for in an averaged manner, for example, if a moleule is embedded into a polarizable medium. Arguments are given in favor of the perturbational solution which facilitate the treatment of nonlinearity effects. Two examples are discussed: the case of a polarizable environment and the effective correction of the basis set superposition error.

1.   Introduction

In the theory of the molecular electronic structure, one mostly deals with the nonrelativistic time-independent Schrödinger equation

$$H\Psi = E\Psi, \tag{1}$$

where H is the Born–Oppenheimer electronic Hamiltonian. This equation is linear since H is a linear operator:

$$H(\alpha\Psi + \beta\Phi) = \alpha H\Psi + \beta H\Phi. \tag{2}$$

There are, however, some applications in which the Hamiltonian is not a linear operator and it does not obey eq. (2). This nonlinearity occurs, for example, if the Hamiltonian H depends on the wave function Ψ:

$$H = H(\Psi) \tag{3}$$

and the Schrödinger equation reads:

$$H(\Psi)\Psi = E\Psi. \tag{4}$$

In the general case, this equation cannot be deduced as a stationary solution of the time-dependent Schrödinger equation

$$H(\Phi)\Phi = \frac{\hbar}{i} \frac{\partial}{\partial t} \Phi,$$

but should be considered only as a model. However, in the cases analyzed in this paper, the Hamiltonian depends on Φ through an expectation value:

$$H(\Phi) = H^0 + \langle \Phi | \hat{A} | \Phi \rangle \hat{B},$$

where $\hat{A}$ and $\hat{B}$ are two operators defined by the model in question. Then, in the stationary case eq. (4) is recovered for Ψ by the substitution $\Phi(t) = \Psi e^{i\omega t}$.

Nonlinear Schrödinger equations are dealt with in various fields of physics; we mention the theory of Heisenberg ferromagnets [1–3], soliton dynamics [4–6], or the interactions with the radiation field [7,8]. In this paper, we shall consider a different problem, in which the nonlinearity of the *time-independent* Schrödinger equation is a consequence of intermolecular interactions, either because they are accounted for in an averaged manner leading to solvation models [9–12], or because some part of the many-body interaction Hamiltonian is artificially averaged in order to avoid the basis set superposition error (BSSE) [13,14].

2. General considerations

In many actual models, the nonlinear Hamiltonian can be written in the form:

$$H = H^0 + V(\Psi), \tag{5}$$

while the Schrödinger equation for the state K becomes

$$\left(H^0 + V(\Psi_K)\right)\Psi_K = E_K \Psi_K. \tag{6}$$

Solution of eq. (6), in principle, is possible in several ways:

(i) *Iterative solution.* The most straightforward idea is to start by solving

$$H^0 \Psi_K^0 = E_K^0 \Psi_K^0, \tag{7}$$

then construct an approximate potential $V(\Psi_K^0)$, solve (6), construct V by the new solution, and iterate until self-consistency. In addition to possible convergence difficulties, the disadvantages of this technique are that it does not lead to easily interpretable interaction terms, and it should be repeated for each state K from the very beginning.

(ii) *Conventional quantum chemical techniques,* e.g. configuration interaction (CI), are not trivial to implement because the Hamiltonian depends on the state K.

(iii) *Variational procedures* cannot be based on the usual Rayleigh quotient $\langle \Psi \mid H \mid \Psi \rangle / \langle \Psi \mid \Psi \rangle$ as the variational functional, because its stationary points do not provide the eigenfunctions of the Hamiltonian $H(\Psi)$ [10].

(iv) *Perturbational techniques* should also be modified since in standard procedures one considers only a linear perturbation as $H = H^0 + \lambda W$, while, due to the wave function dependency, expansion of eq. (6) yields

$$H = H^0 + \lambda V^0 + \lambda^2 V^1 + \lambda^3 V^2 + \dots , \tag{8}$$

where λ is a formal perturbation parameter characterizing the perturbation strength. Effects of V^k for $k > 0$ on the perturbation corrections are the subject of a special perturbation theory (PT) which will be developed in the following section. It is obvious that the PT may also suffer from serious convergence difficulties for large perturbations. In the present paper, in sections 4 and 5, we shall apply such PT to account for intermolecular interactions which are supposed to be weak enough to justify a perturbational treatment.

3. PT for nonlinear Schrödinger equations

Consider the Hamiltonian with nonlinear perturbations, cf. eq. (8):

$$H = H^0 + \sum_{\mu=1}^{\infty} \lambda^\mu V^{\mu-1} \tag{9}$$

and the Schrödinger equation

$$H\Psi = E\Psi. \tag{10}$$

Expanding Ψ and E into a perturbational series according to the parameter λ, one obtains

$$\Psi_K = \sum_{\mu=0}^{\infty} \lambda^\mu \Psi_K^\mu , \tag{11a}$$

$$E_K = \sum_{\mu=0}^{\infty} \lambda^\mu E_K^\mu . \tag{11b}$$

Substituting these expansions into the Schrödinger equation (10), one can write

$$\sum_{\mu=0}^{\infty} \lambda^\mu H^0 \Psi_K^\mu + \sum_{\tau=1}^{\infty} \sum_{\mu=0}^{\infty} \lambda^{\mu+\tau} V^{\tau-1} \Psi_K^\mu = \sum_{\mu\nu=0} \lambda^{\mu+\nu} E_K^\mu \Psi_K^\nu . \tag{12}$$

Collecting here all terms of a given order in λ, one obtains the perturbation equation for that order. At the zeroth order, one easily recovers eq. (7). At the first order, the following result is obtained:

$$H^0 \Psi_K^1 + V^0 \Psi_K^0 = E_K^0 \Psi_K^1 + E_K^1 \Psi_K^0 , \tag{13}$$

from which we get for the first-order energy

$$E_K^1 = \langle \Psi_K^0 | V^0 | \Psi_K^0 \rangle, \tag{14}$$

which trivially matches the usual result of the Rayleigh–Schrödinger (RS) PT, since nonlinearity can affect the results only from the second order on. At the second order, one finds

$$H^0 \Psi_K^2 + V^0 \Psi_K^1 + V^1 \Psi_K^0 = E_K^2 \Psi_K^0 + E_K^1 \Psi_K^1 + E_K^0 \Psi_K^2 ; \tag{15}$$

by means of which the second-order energy is

$$E_K^2 = \langle \Psi_K^0 | V^0 | \Psi_K^1 \rangle + \langle \Psi_K^0 | V^2 | \Psi_K^0 \rangle. \tag{16}$$

This result is different from the standard RS–PT formula (first term) in the presence of the expectation value of the second-order interaction (second term). At the general order n, collecting all the nth-order terms in eq. (12), one obtains:

$$\left(H^0 - E_K^0 \right) \Psi_K^n + \sum_{\mu=0}^{n-1} V^{n-\mu-1} \Psi_K^\mu = \sum_{\mu=1}^{n} E_K^\mu \Psi_K^{n-\mu}. \tag{17}$$

From this perturbation equation, the nth-order energy correction can be obtained by multiplying it with $\langle \Psi_K^0 |$:

$$E_K^n = \sum_{\mu=0}^{n-1} \langle \Psi_K^0 | V^{n-\mu-1} | \Psi_K^\mu \rangle, \tag{18}$$

which is a general result in a recursive form. It is to be compared with the usual RS result

$$E_K^n = \langle \Psi_K^0 | V^0 | \Psi_K^{n-1} \rangle, \tag{19}$$

which corresponds to the last term of the sum in eq. (18). As to the wave function corrections at the general order n, they are obtained from eq. (17) by expanding them according to the zeroth-order states:

$$\Psi_K^n = \sum_{K \neq L} C_{KL}^n \Psi_L^0 \tag{20}$$

and multiplying (17) by $\langle \Psi_J^0 |$ for $J \neq K$. For the unknown coefficients C_{KJ}^n, one obtains the following result:

$$C_{KJ}^n = \frac{\sum\limits_{\mu=1}^{n} E_K^\mu C_{KJ}^{n-\mu} - \sum\limits_{L \neq K} \sum\limits_{\mu=0}^{n-1} C_{KL}^\mu V_{JL}^{n-\mu-1}}{E_J^0 - E_K^0}. \tag{21}$$

Equations (18) and (21) represent the general solutions of the nonlinear perturbation problem at the arbitrary order n, in the form of a recursive relation containing contributions from the previous orders $\mu < n$. Application of this general result will be presented in the forthcoming sections.

4. Molecule in a polarizable medium [12]

A special case of the nonlinear PT developed in the previous section was published some years ago [12]. We summarize it briefly because of its significance in quantum chemical calculations of solvatation energies.

If we consider a molecule being embedded into a polarizable medium, the appropriate model Hamiltonian of the system can be obtained by focusing on the molecule and modifying its Hamiltonian incorporating the interaction with the environment in an effective manner. In the most usual model, only dipole–dipole interactions are considered (Onsager cavity model [15]):

$$H = H^0 + \lambda M \langle \Psi | M | \Psi \rangle, \tag{22}$$

where M is the dipole moment operator and λ is the perturbation parameter depending on the dielectric constant ε of the medium and on the radius of the cavity a, a parameter of the model:

$$\lambda = -\frac{2(\varepsilon-1)}{2\varepsilon+1} (a_0/a)^3, \tag{23}$$

where a_0 is the Bohr radius. Expanding Ψ according to λ via eq. (11a) and substituting this into eq. (22), we get for the nonlinear Hamiltonian

$$H = H^0 + \sum_{\mu, \nu=0}^{\infty} \lambda^{\mu+\nu} M \langle \Psi^\mu | M | \Psi^\nu \rangle. \tag{24}$$

Identifying the terms at various powers of λ, one obtains

$$V^0 = M\langle\Psi^0|M|\Psi^0\rangle,$$

$$V^1 = M\langle\Psi^0|M|\Psi^1\rangle + M\langle\Psi^1|M|\Psi^0\rangle,$$

$$V^2 = M\langle\Psi^0|M|\Psi^2\rangle + M\langle\Psi^1|M|\Psi^1\rangle + M\langle\Psi^2|M|\Psi^0\rangle, \tag{25}$$

and so on. Substituting these terms into the general results of the preceding section, one obtains a recursive relation for the eigenvectors and the eigenvalues [12]. Defining the self-energy of the molecule as

$$\mathcal{E} = E^0 + \tfrac{1}{2}E^{int},$$

where E^{int} is the interaction energy, half of which is spent by the molecule to polarize its environment [16], one gets the following result for the state K

$$\mathcal{E}_K = E^0 - \tfrac{1}{2}M_{KK}R_K - \tfrac{3}{4}\alpha_K R_K^2 + \ldots, \tag{26}$$

where M_{KK} is the matrix element of the dipole moment operator, while R_K is the reaction field defined as

$$R_K = -\lambda/a_0^3\, M_{KK},$$

with the λ defined in eq. (23). Equation (26) is easy to interpret: the first term on the r.h.s. is the energy of the molecule in vacuo, the second term describes the static dipole–dipole interaction, while the third term gives the interaction of the induced dipole moment of the molecule with the reaction field. Higher-order terms come from the changes of the reaction field itself.

5.   A BSSE-free perturbation theory for intermolecular interactions

Now we are going to present a quite different situation where a nonlinear Schrödinger equation of type (6) emerges. The problem addressed here is that of the so-called basis set superposition error (BSSE), which occurs if calculating energy differences obtained in different basis sets. Basically, it is topical in the field of intermolecular interactions where the interaction energy between molecules A and B is, in principle, defined by

$$\Delta E = E_{AB} - E_A - E_B. \tag{27}$$

Here, E_{AB} is the energy of the supersystem, E_A and E_B are those of the isolated systems A and B, respectively. The problem emerges if these three quantities are not computed exactly, but are obtained approximately by expanding the wave functions

in finite (incomplete) basis sets. In such a case, in calculating the dimer energy E_{AB}, the basis sets used for A and B are merged; thus, the dimer is described in a larger (more flexible) basis as compared to the monomers. The lack of balance of the basis sets introduces an artificial error in the interaction energy if eq. (27) is used. This error is called the BSSE (see [17] and references therein).

Methods to correct for BSSE can be classified into two groups:

(i) One may try to modify the basis sets for the monomers A and B to approach the quality of the dimer basis [18,19]. These methods can give quite balanced results, especially the so-called Boys–Bernardi scheme [18], where the monomers are calculated in the full dimer basis set. The disadvantages are that one has to repeat, besides the dimer calculation, both monomer calculations at each intermolecular configuration when scanning a potential surface, and the dimer basis does not reflect the symmetry of the monomer. Moreover, it can be shown [19] that the BSSE is not an additive error, thus is cannot be exactly corrected by simply readjusting the monomer energies.

(ii) One may try to extract the physical term from E_{AB} containing only the relevant interaction. This requires a thorough theoretical analysis of the dimer Hamiltonian. An important step in this direction is the many-body theory of Mayer, called the chemical Hamiltonian approach (CHA) [13,14,21,22]. There is no room here to review this involving and general approach. We mention only that in connection with intermolecular interactions, the basic result of the theory is a unique partitioning of the many-body (second quantized) Hamiltonian H_{AB} for the dimer

$$H_{AB} = H_A + H_B + W + B, \tag{28}$$

where H_A and H_B are the second quantized effective monomer Hamiltonians which act on the dimer basis, but their left eigenvectors are the isolated molecule wave functions. W is an expression of the true physical interaction, while the rest of the dimer Hamiltonian B results from the incompleteness of the basis set and can be considered as a BSSE term. One also finds that the operator W is the second quantized representant of the interaction operator written in the L_2 space [23].

In our laboratory [13,14,23–28], we have performed numerical calculations using only W as the interaction operator. That is, we considered the model Hamiltonian

$$H_{AB}^{phys} = H_A + H_B + W \tag{29}$$

and solved our supermolecule problem either variationally or perturbatively with respect to this Hamiltonian. H_{AB} and H_{AB}^{phys} become equivalent in complete basis sets. In usual standard bases of quantum chemistry, however, it was found that these results differ considerably. Neither the results obtained by H_{AB} nor those obtained by H_{AB}^{phys} were good as compared to experimental potential curves or more sophisticated calculations. The former exhibited artifact BSSE, while the latter were quite unstable, usually showing a lack of overlap repulsion. It was also found, however, that solving the BSSE-free Schrödinger equation

$$H_{AB}^{phys}\, \Psi^{phys} = \mathcal{E}\, \Psi^{phys} \tag{30}$$

but calculating the dimer energy with the full Hamiltonian as

$$E_{AB} = \frac{\langle \Psi^{phys}|H_{AB}|\Psi^{phys}\rangle}{\langle \Psi^{phys}|\Psi^{phys}\rangle}, \tag{31}$$

one obtains superior results for the dimer energy. This was called the CHA/CE (chemical Hamiltonian with conventional energy) method.

The CHA/CE method has been tested in several applications and it turned out that the CHA/CE potential curves are quite close to those obtained by the Boys–Bernardi procedure. This is a very useful achievement since the CHA/CE results are obtained at the expense of a single calculation at each intermolecular configuration. Consequently, one could suggest it to be a standardized technique for calculating intermolecular interaction energies.

There is one point, however, which requires further analysis. Namely, a formal objection against the CHA/CE procedure is that the wave function is obtained by a Hamiltonian (eq. (30)) which is different from that used in the energy expression eq. (31). This is a consequence of the fact that, as could be learned from the success of the CHA/CE method, the *BSSE is present in the wave function* and not in the Hamiltonian part of the energy expression. This confirms the idea that BSSE is an artifact delocalization component of the wave function.

The formal objection against using two different Hamiltonians can be corrected, again formally, in the following manner. Consider the Schrödinger equation

$$[H_{AB}^{phys} + |\Psi\rangle\langle\Psi|B]|\Psi\rangle = E|\Psi\rangle. \tag{32}$$

This formal nonlinear equation has the property that the eigenfunction Ψ is an eigenfunction of H^{phys}, and the eigenvalue E is

$$E = \frac{\langle\Psi|H_{AB}^{phys}|\Psi\rangle + \langle\Psi|B|\Psi\rangle}{\langle\Psi|\Psi\rangle} = \frac{\langle\Psi|H_{AB}|\Psi\rangle}{\langle\Psi|\Psi\rangle}. \tag{33}$$

Thus, both eqs. (30) and (31) are fulfilled. We note that a summation over states is to be introduced into eq. (32) if excited states are also of interest.

The perturbation theory for the nonlinear Schrödinger equation (32) can be developed analogously to the PT in the previous section. The Hamiltonian H^{phys} is split into a zeroth-order part and a physical interaction:

$$H^{phys} = H^0 + \lambda W. \tag{34}$$

If the wave function and the energy are expanded as in eqs. (11) and (20), and the expansions are substituted into the Schrödinger equation (32), one obtains

$$\sum_{\mu=0}^{\infty} \lambda^{\mu} \sum_{i} C_i^{\mu} H^0 |\Psi_i^0\rangle + \sum_{\mu=0}^{\infty} \lambda^{\mu+1} \sum_{i} C_i^{\mu} W |\Psi_i^0\rangle$$

$$+ \sum_{\mu\nu\rho=0}^{\infty} \lambda^{\mu+\nu+\rho+1} \sum_{ijk} C_i^{\mu} C_j^{\nu} C_k^{\rho} \langle\Psi_i^0 | B | \Psi_i^0\rangle |\Psi_k^0\rangle = \sum_{\mu\nu=0}^{\infty} \lambda^{\mu+\nu} E_0^{\mu} \sum_{i} C_i^{\nu} |\Psi_i^0\rangle.$$

Assuming the hermiticity of the zeroth-order Hamiltonian, and using that the zeroth-order functions are eigenfunctions of H^0, one obtains from the above equation for the various orders

$$E_0^1 = W_{00} + B_{00}, \tag{35a}$$

$$E_0^2 = -\sum_{i} \frac{(W_{0i} + B_{0i} + B_{i0})W_{i0}}{E_i^0 - E_0^0}, \tag{35b}$$

and for the general order n, one obtains the recursive relation

$$E_0^n = \sum_{i} C_i^{n-1} W_{0i} + \sum_{\mu=0}^{n-1} \sum_{ij} C_i^{\mu} C_j^{n-\mu-1} B_{ij}, \tag{36}$$

while for the wave function correction, one obtains

$$C_l^n = -\sum_{i} \frac{C_i^{n-1} W_{li}}{E_l^0 - E_0^0} + \sum_{\mu=1}^{n-1} E_0^{\mu} \frac{C_l^{n-\mu}}{E_l^0 - E_0^0} - \sum_{\mu\nu}^{\mu+\nu\leq n-1} \sum_{ij} \frac{C_i^{\mu} C_j^{\nu} C_l^{n-\mu-\nu} B_{ij}}{E_l^0 - E_0^0}. \tag{37}$$

In eqs. (36) and (37), the last terms represent the nonlinearity effects which are now due to the operator B describing the incompleteness of the basis set. The rest of the terms are identical to those of the usual Rayleigh–Schrödinger PT.

The significance of the second-order result (eq. (35b)) is worth mentioning. In a standard many-body approach without taking any care of the BSSE problem, the physical interaction operator W and the finite basis correction term B are handled on an equal footing. If this were the case, one would get

$$E_0'^2 = -\sum_{K} (W + B)_{0K}(W + B)_{K0} / \Delta E_{0K} = E_0^2 - \sum_{K} B_{K0} B_{0K} / \Delta E_{0K}.$$

Accordingly, the message of the present theory is that pure BSSE terms are to be excluded from the second-order correction of the interaction energy, but the interference (cross-) terms between W and B are to be kept in order to obtain reliable results.

In actual applications, the zeroth-order Hamiltonian is not Hermitian, which causes some changes in the perturbation formulae. These, together with some numerical applications to test low-order corrections, will be presented elsewhere [29].

One of the messages of this paper is that quite different problems in the field of intermolecular interactions (namely, the embedding of a molecule into a solvent and the BSSE problem) can be treated in a mathematically closely related manner. No matter what makes the model Schrödinger equation nonlinear, one can develop general solution techniques on an equal footing.

Acknowledgements

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