NONLINEAR SCHRODINGER 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 molecule 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

$$H \Psi = E \Psi,$$

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

$$H(\alpha \Psi + \beta \Phi) = \alpha H \Psi + \beta H \Phi.$$  \hspace{1cm} (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 $\Psi$:

$$H = H(\Psi)$$ \hspace{1cm} (3)

and the Schrödinger equation reads:

$$H(\Psi) \Psi = E \Psi.$$ \hspace{1cm} (4)

In the general case, this equation cannot be deduced as a stationary solution of the time-dependent Schrödinger equation.
but should be considered only as a model. However, in the cases analyzed in this paper, the Hamiltonian depends on \( \Phi \) 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 \( \Psi \) 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:

\[
H = H^0 + V(\Psi),
\]

while the Schrödinger equation for the state \( K \) becomes

\[
(H^0 + V(\Psi_K))\Psi_K = E_K \Psi_K.
\]

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

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

\[
H^0 \Psi_K^0 = E_K^0 \Psi_K^0,
\]

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 \( K \).