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Two new symmetry-adapted perturbation theories for the calculation of intermolecular interaction energies

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Abstract. We outline two new symmetry-adapted perturbation theories (SAPTs) and present some results obtained with them. The first is superior to the symmetrized Rayleigh–Schrödinger (SRS) theory in that it corrects a fundamental defect of that theory, namely, that carried to infinite order the SRS theory cannot predict even the ground-state energy for most interacting atoms and molecules. The new theory includes correction terms which have a large cumulative effect, but which, order by order, make only small contributions. When applied to interacting closed-shell systems and truncated after first order in the wave function, it is equal in accuracy to the SRS theory. Thus, it provides both an understanding of why the SRS theory gives results of useful accuracy and justification for its continued use when truncated to low order. The second new SAPT also corrects the SRS theory’s flaw, but achieves significantly greater accuracy than the SRS theory when truncated after first order in the wave function. Applied to the interaction between the open-shell Li and H atoms, a critical test case, the second theory gives the ground-state dissociation energy with an error of 1%, whereas the SRS theory is in error by 38%. The LiH molecule is a critical test case because its physical ground-state energy, like that of nearly all systems, lies in a continuum of accessible states which violate the Pauli exclusion principle.

Key words: Symmetry-adapted perturbation theory – Intermolecular potential energies – Pauli forbidden states

1 Introduction

We outline two new perturbation theories for the calculation of intermolecular energies. The first is fundamentally superior to the symmetrized Rayleigh–Schrödinger (SRS) perturbation theory [1, 2], a theory that has given interaction energies of good accuracy for a variety of systems and that has been implemented in a computer program of general utility [3]. The second, a refinement of the first, is fundamentally and numerically superior to the SRS theory.

The SRS theory is the polarization approximation (PA) [4] plus an energy formula. For simplicity of exposition we consider a diatomic system A–B. Its nonrelativistic Schrödinger Hamiltonian, \( \hat{H} \), is split into two parts. One part, \( \hat{H}^o \), is the sum of the A-atom Hamiltonian and the B-atom Hamiltonian with electrons \( N_A \) and \( N_B \) assigned specifically to A, and \( N_A + 1 \) to \( N = N_A + N_B \) assigned to B. The unperturbed Hamiltonian is \( \hat{H}^o \) and the perturbation is \( \hat{V} = \hat{H} - \hat{H}^o \). The basic idea of the PA theory is to solve

\[
(\hat{H}^o + \lambda \hat{V})F(\lambda) = \delta(\lambda)F(\lambda)
\]

by Rayleigh–Schrödinger perturbation theory, obtaining \( F(\lambda) \) and \( \delta(\lambda) \) as power series in \( \lambda \). When \( \lambda = 0 \) Eq. (1) describes the noninteracting atoms, when \( \lambda = 1 \), the interacting atoms. The SRS theory defines the interaction energy by

\[
\Delta\delta(\lambda) = \lambda\langle F^o | \hat{V} \sigma | F(\lambda) \rangle / \langle F^o | \sigma | F(\lambda) \rangle ,
\]

where \( \sigma \) is the totally antisymmetric projection operator and \( F(\lambda) \) is the solution to Eq. (1) for which \( F(0) = F^o \), the lowest eigenfunction of \( \hat{H}^o \).

The PA/SRS theory has a fundamental flaw. The Schrödinger equation has physical and unphysical solutions. The latter violate the Pauli exclusion principle (PEP). Let the physical eigenfunctions and eigenvalues of \( \hat{H} \) be \( \Phi_k \) and \( E_k \), respectively, ordered so that \( E_k \leq E_{k+1} \). The unphysical eigenfunctions and eigenvalues are \( \Phi_k^u \) and \( E_k^u \), ordered so that \( E_k^u \geq E_{k+1}^u \). When \( A-B \) has more than two electrons \( E_{i}^u \) lies below the physical ground-state energy, \( E_{i} \) [5]. When one or both atoms have an atomic number greater than 2, \( E_{i} \) generally lies in a continuum of unphysical energies [6]. Below the continuum are an infinite number of discrete unphysical energies. It is the overlapping of the physical and unphysical energy spectra that makes the PA expansion generally divergent and makes the SRS theory fundamentally unsound.
One needs to understand how the PA/SRS theory is fundamentally unsound to understand that the new theories are sound. The eigenvalue $\delta(\lambda)$ of Eq. (1) is best understood as a Riemann surface, a multivalued function of the complex variable $\lambda$ [7]. The Riemann surface consists of many sheets, $\delta_j(\lambda)$, ordered by their real parts so that $\Re \delta_j(\lambda) < \Re \delta_{j+1}(\lambda)$. The lowest unperturbed energy lies on the lowest sheet, i.e., $\delta_1(0) = \delta^\circ$. The PA and SRS theories assume incorrectly that $\delta_1(1) = \delta^\circ$, the physical ground-state energy. Generally, $\delta_1(1)$ equals the lowest unphysical energy, $E^T_1$ [5]. If $E_1$ lies on a sheet $\delta_j(\lambda)$ of the same Riemann surface as $\delta^\circ$, one can imagine analytically continuing from $\delta_1(\lambda)$ to $\delta_j(\lambda)$ via the intervening sheets [7]. The index $J$ is indeterminately large for most systems. Thus, the PA theory yields an indeterminately large number of unphysical solutions before it yields the physical ground-state solution. Consequently, the SRS theory cannot predict for most systems even the physical ground-state energy when carried to infinite order [8]. It is, however, reasonably accurate when truncated after first order in the wave function.

A number of alternatives to the PA and SRS theories have been proposed, but only a few are well understood mathematically. These are the Eisenschitz–London–van der Avoird–Hirschfelder (EL-HAV) [9, 10, 11], Amos–Musher (AM) [12, 13], Polymeropoulos–Adams (AP) [14] and Hirschfelder–Silbey (HS) theories [15, 16]. The EL-HAV, AM and AP theories have no unphysical energies below the physical ground-state energy for attractive interactions and, consequently, are capable, in principle, of predicting the physical ground-state energy exactly. Unfortunately, they share a practical defect: to second order in $\lambda$ the interaction energy they predict is only a fraction of the asymptotic value at large separations, $R$. In contrast, the unsound SRS theory, to the same order, predicts the asymptotic dependence on $1/R$ exactly.

The HS theory is designed to predict correctly the asymptotic $1/R$ dependence at second order. Because of this, one can argue that it is the correct theory for calculating interaction energies [17]. Conversely, one can argue that the HS theory must be as unsound as the SRS theory because it leaves the physical ground-state energy buried in the continuum of unphysical energies [18]. Consistent with the latter argument are recent results for Li interacting with H. The HS expansion for LiH diverges at $\lambda = 1$ and is numerically no more accurate than the simpler SRS theory when truncated to the same order [19].

These observations suggest that a satisfactory perturbation theory for intermolecular energies has yet to be proposed. This is unsurprising because all the theories cited were proposed before it was recognized that the physical ground-state energy generally lies in a continuum of unphysical energies. A recently proposed theory [20], however, may prove to be satisfactory. Because it has an essential element in common with ours, we discuss it in the last section.

We have designed the new symmetry-adapted perturbation theory (SAPT) in light of what was learned from previous ones. Foremost, was that they could be understood to infinite order if their starting points were eigenproblems. In addition, $F$, the lowest energy solution of the eigenproblem, should be simply related to the ground-state function, $\Phi_1$, and, at infinite separation, equals $F^\circ$. There is a general method for constructing an eigenproblem which has an eigenfunction, $F$, with the properties that $\mathcal{A} F \propto \Phi_1$ and that $F$ minimizes the expectation value of a reference Hamiltonian, $\mathcal{H}^\bullet$ [21]. By setting $\mathcal{H}^\bullet = \mathcal{H}$ one gets the AP eigenproblem, which, by approximation, becomes the AM equation $(\mathcal{H}^\circ + \lambda \mathcal{A} V) F(\lambda) = \delta(\lambda) F(\lambda)$ [22]. The AM-AP theories shift the energies of unphysical solutions above the ground-state energy for attractive interactions and largely eliminate the unphysical energies as a problem. Unfortunately, they badly underestimate the asymptotic dependence of the energy on $1/R$ when $F(\lambda)$ is truncated after first order. Thus, the question is whether there is there a better choice for $\mathcal{H}^\bullet$.

Our new choice for $\mathcal{H}^\bullet$ is based on two observations. The first is that the lowest unphysical states generally arise from one or more valence electrons of an atom falling into the core of its neighbor. This would not happen if the nuclear Coulomb potentials in $\mathcal{V}$ were less strong near the nuclei. We weaken them by subtracting a potential $\bar{u}$. The second observation is that if $\bar{u}$ is short ranged it will have no effect on the asymptotic properties of the energy because those properties depend on the nuclear Coulomb potentials far from the nuclei. We set $\mathcal{H}^\bullet = \mathcal{H} - \bar{u} = \mathcal{H}^\circ + \mathcal{V} - \bar{u}$. We define $\bar{u}$ explicitly in Sect. 2. It belongs to a class of potentials considered formally by Herring in discussing the long-range coupling of spins [23].

2 A new starting point

For brevity we simply write down the eigenproblem that serves as our starting point, establish its properties and define $\bar{u}$. The method of derivation is explained elsewhere [22]. The eigenproblem is

$$[\mathcal{H}^\circ + \mathcal{V} - \bar{u} + \mathcal{A}(\bar{u} - D)] F_1 = \delta_1 F_1 ,$$

where $D$ is a real numerical constant. Its optimum value for the ground state,

$$D = \langle F_1 | \mathcal{A} \bar{u} | F_1 \rangle / \langle F_1 | \mathcal{A} | F_1 \rangle ,$$

makes $F_1$ least distorted from the lowest eigenfunction of $\mathcal{H}^\bullet$ [21]. To linearize Eq. (3), however, we define $D$ somewhat differently for each SAPT, namely, we substitute the unperturbed wave function for $F_1$ in Eq. (4).

The solutions of Eq. (3) can be divided into two classes. One class has the property $\mathcal{A} F_k = 0$, i.e., the functions are purely unphysical. We write $F^\nu_k$ for these functions and $\delta^\nu_k$ for their eigenvalues to distinguish them from those for which $\mathcal{A} F_k \neq 0$, i.e., functions which have a physical component.

Consider first the $F_k$ which have a physical component. Multiply Eq. (3) from the left by $\mathcal{A}$. The expression is simplified by using $\mathcal{A}^{\perp} = \mathcal{A}$ and $\mathcal{A} (\mathcal{H}^\circ + \mathcal{V}) = (\mathcal{H}^\circ + \mathcal{V}) \mathcal{A}$. The result is