Theor Chem Acc (2002) 108:225–231
DOI 10.1007/s00214-002-0377-3

Theoretical
Chemistry Accounts

Regular article

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

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Received: 22 May 2002 / Accepted: 26 June 2002 /

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, $\hat{H}^\circ$, is the sum of the A-atom Hamiltonian and the B-atom Hamiltonian with electrons 1 to N_A assigned specifically to A, and $N_\mathrm{A}+1$ to $N = N_\mathrm{A} + N_\mathrm{B}$ assigned to B. The unperturbed Hamiltonian is $\hat{H}^\circ$ and the perturbation is $\hat{V} = \hat{H} - \hat{H}^\circ$. The basic idea of the PA theory is to solve

$$\left(\hat{H}^\circ + \lambda\hat{V}\right)F(\lambda) = \mathscr{E}(\lambda)F(\lambda) \tag{1}$$

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

$$\Delta\mathscr{E}(\lambda) = \lambda\left\langle F^\circ\middle|\hat{V}\hat{\mathscr{A}}\middle|F(\lambda)\right\rangle / \left\langle F^\circ\middle|\hat{\mathscr{A}}\middle|F(\lambda)\right\rangle\ , \tag{2}$$

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

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 Φ_k and E_k, respectively, ordered so that $E_\mathrm{k} \leq E_{\mathrm{k}+1}$. The unphysical eigenfunctions and eigenvalues are Φ_k^u and E_k^u, ordered so that $E_k^\mathrm{u} \leq E_{k+1}^\mathrm{u}$. When A–B has more than two electrons E_1^u lies below the physical ground-state energy, E_1 [5]. When one or both atoms have an atomic number greater than 2, E_1 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.

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One needs to understand how the PA/SRS theory is fundamentally unsound to understand that the new theories are sound. The eigenvalue $\mathscr{E}(\lambda)$ of Eq. (1) is best understood as a Riemann surface, a multivalued function of the complex variable λ [7]. The Riemann surface consists of many sheets, $\mathscr{E}_j(\lambda)$, ordered by their real parts so that $\Re\mathscr{E}_j(\lambda) \leq \Re\mathscr{E}_{j+1}(\lambda)$. The lowest unperturbed energy lies on the lowest sheet, i.e., $\mathscr{E}_1(0) = \mathscr{E}^\circ$. The PA and SRS theories assume incorrectly that $\mathscr{E}_1(1) = E_1$, the physical ground-state energy. Generally, $\mathscr{E}_1(1)$ equals the lowest unphysical energy, E_1^{u} [5]. If E_1 lies on a sheet $\mathscr{E}_J(\lambda)$ of the same Riemann surface as $\mathscr{E}^\circ$, one can imagine analytically continuing from $\mathscr{E}_1(\lambda)$ to $\mathscr{E}_J(\lambda)$ 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 λ 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, Φ_1, and, at infinite separation, equals F°. There is a general method for constructing an eigenproblem which has an eigenfunction, F, with the properties that $\hat{\mathscr{A}}F \propto \Phi_1$ and that F minimizes the expectation value of a reference Hamiltonian, $\hat{H}^\bullet$ [21]. By setting $\hat{H}^\bullet = \hat{H}^\circ$ one gets the AP eigenproblem, which, by approximation, becomes the AM equation $\left(\hat{H}^\circ + \lambda\hat{\mathscr{A}}\hat{V}\right)F(\lambda) = \mathscr{E}(\lambda)F(\lambda)$ [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 $\hat{H}^\bullet$.

Our new choice for $\hat{H}^\bullet$ 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 $\hat{V}$ were less strong near the nuclei. We weaken them by subtracting a potential $\hat{u}$. The second observation is that if $\hat{u}$ 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 $\hat{H}^\bullet = \hat{H} - \hat{u} = \hat{H}^\circ + \hat{V} - \hat{u}$. We define $\hat{u}$ 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 $\hat{u}$. The method of derivation is explained elsewhere [22]. The eigenproblem is

$$\left[\hat{H}^\circ + \hat{V} - \hat{u} + \hat{\mathscr{A}}(\hat{u} - D)\right]F_k = \mathscr{E}_k F_k \ , \tag{3}$$

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

$$D = \left\langle F_1 \middle| \hat{\mathscr{A}}\hat{u} \middle| F_1 \right\rangle / \left\langle F_1 \middle| \hat{\mathscr{A}} \middle| F_1 \right\rangle \ , \tag{4}$$

makes F_1 least distorted from the lowest eigenfunction of $\hat{H}^\bullet$ [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 $\hat{\mathscr{A}}F_k = 0$, i.e., the functions are purely unphysical. We write F_k^{u} for these functions and $\mathscr{E}_k^{\mathrm{u}}$ for their eigenvalues to distinguish them from those for which $\hat{\mathscr{A}}F_k \neq 0$, 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 $\hat{\mathscr{A}}$. The expression is simplified by using $\hat{\mathscr{A}}^2 = \hat{\mathscr{A}}$ and $\hat{\mathscr{A}}\left(\hat{H}^\circ + \hat{V}\right) = \left(\hat{H}^\circ + \hat{V}\right)\hat{\mathscr{A}}$. The result is

$$\left(\hat{H}^\circ + \hat{V} - D\right)\hat{\mathscr{A}}F_k = \mathscr{E}_k\hat{\mathscr{A}}F_k \ . \tag{5}$$

Thus, if $\hat{\mathscr{A}}F_k \neq 0$, $\hat{\mathscr{A}}F_k$ must be a physical eigenfunction of $\hat{H} = \hat{H}^\circ + \hat{V}$. Therefore,

$$\hat{\mathscr{A}}F_k \propto \Phi_k \quad \text{and} \quad \mathscr{E}_k = E_k - D \ . \tag{6}$$

Thus, the physical energies are given exactly by Eq. (3). Note, too, that the $\mathscr{E}_k$ are real if D is real.

We are also interested in the purely unphysical solutions to Eq. (3). Add a superscript u to F_k and $\mathscr{E}_k$ in Eq. (3), then multiply from the left by $1 - \hat{\mathscr{A}}$, substituting the identity $F_k^{\mathrm{u}} = \left(1 - \hat{\mathscr{A}}\right)F_k^{\mathrm{u}}$ to get

$$\left(1 - \hat{\mathscr{A}}\right)\left(\hat{H}^\circ + \hat{V} - \hat{u}\right)\left(1 - \hat{\mathscr{A}}\right)F_k^{\mathrm{u}} = \mathscr{E}_k^{\mathrm{u}}\left(1 - \hat{\mathscr{A}}\right)F_k^{\mathrm{u}} \ . \tag{7}$$

Thus, the $\mathscr{E}_k^{\mathrm{u}}$ are real if $\hat{u}$ is Hermitian. We define $\hat{u}$ later so that $\mathscr{E}_1^{\mathrm{u}}$, the lowest eigenvalue of Eq. (7), is greater than E_1–D. This eliminates the unphysical energies as a major impediment to the development of a fundamentally sound SAPT.

Because $\hat{u}$ is to cancel to some degree the nuclear Coulomb potentials in $\hat{V}$, we give it a similar structure. The potential $\hat{V} = \hat{v}_{\mathrm{B}}^{\mathrm{A}} + \hat{v}_{\mathrm{A}}^{\mathrm{B}} + \hat{g}$, where $\hat{g}$ is the Coulomb potential energy of the A electrons interacting with the B electrons and $\hat{v}_{\mathrm{B}}^{\mathrm{A}}$ is the potential energy of the B electrons in the field of the A nucleus, i.e., $\hat{v}_{\mathrm{B}}^{\mathrm{A}} = -Z_{\mathrm{A}}\sum_{j\in\mathrm{B}} 1/r_{\mathrm{A}j}$. We define

$$\hat{u} = \hat{u}_{\mathrm{B}}^{\mathrm{A}} + \hat{u}_{\mathrm{A}}^{\mathrm{B}} \quad \text{and} \quad \hat{u}_{\mathrm{B}}^{\mathrm{A}} = -Z_{\mathrm{A}}\sum\nolimits_{j\in\mathrm{B}} \phi(r_{\mathrm{A}j}) \ , \tag{8}$$

where $\phi(r_{\mathrm{A}j})$ is a real, short-range function of $r_{\mathrm{A}j}$, i.e., $\lim_{r_{\mathrm{A}j}\to\infty} r_{\mathrm{A}j}^M\phi(r_{\mathrm{A}j}) = 0$ for all positive M. The only other constraint on the form of ϕ (r) is that it make $\mathscr{E}_1^{\mathrm{u}} > E_1 - D$. The asymptotic $1/R$ dependence of the $\hat{H}^\bullet$ eigenvalues will be the same as those of $\hat{H}$. In addition, the lowest-energy eigenfunction of $\hat{H}^\bullet$ becomes F° in the limit $R = \infty$ [23].

The numerical results we present were obtained using

$$\phi(r) = \begin{Bmatrix} 1/r - 1/c & \text{for } r \leq c, \\ 0 & \text{for } r > c, \end{Bmatrix} \tag{9}$$

where c is a constant characteristic of each atom. When $-Z_{\mathrm{A}}\phi$ (r) is subtracted from $-Z_{\mathrm{A}}/r$ the result is $-Z_{\mathrm{A}}/c$ when $r \leq c$ and $-Z_{\mathrm{A}}/r$ when $r > c$. We also tried exp $(-r/c)/r$, but the results differed insignificantly from those using Eq. (9).

The problem of satisfying the condition $\mathscr{E}_1^{\mathrm{u}} > E_1 - D$ reduces to assigning a value to c for each atom. We choose c_{A} for atom A so that a B electron binds less tightly to A^+ at infinite separation than an A electron. This sets a lower bound for acceptable c_{A} values. There is theoretically no upper bound, but one does not want $\mathrm{c_A}$ to be so large that its value dominates the results. We choose c_{B} analogously. By solving Eq. (7) we have verified that this method of defining the c values works even at separations smaller than R_{e}.

3 Corrected polarization approximation

The starting point for the SRS theory is the Schrödinger eigenproblem. As the starting point for the new SAPT we use Eq. (3), defining D by Eq. (4) with F° substituted for F_1. As in the PA theory $\hat{H}^\circ$ is the zero-order Hamiltonian. The perturbation is then $\hat{\mathscr{V}} = \hat{V} - \hat{u} + \hat{\mathscr{A}}(\hat{u} - D)$. Set $\mathscr{E}(\lambda) = \mathscr{E}^\circ + \sum_{n=1}^{\infty} \lambda^n\mathscr{E}^{(n)}$ and $F(\lambda) = F^\circ + \sum_{n=1}^{\infty} \lambda^n F^{(n)}$, then apply the Rayleigh–Schrödinger theory to

$$\left(\hat{H}^\circ + \lambda\hat{\mathscr{V}}\right)F(\lambda) = \mathscr{E}(\lambda)F(\lambda) \tag{10}$$

to arrive at the set of perturbation equations. We require that $\langle F^\circ|F^\circ\rangle = 1$ and $\langle F^\circ|F(\lambda)\rangle = 1$. The terms in $\hat{\mathscr{V}}$ following $\hat{V}$ may be interpreted as corrections to $\hat{V}$. For this reason we call this SAPT the corrected PA (cPA).

Just as the SRS formula (Eq. 2) to second order is more accurate than the sum of the PA $\mathscr{E}^{(n)}$ to second order, analogous formulas using the cPA function are more accurate than summing the cPA $\mathscr{E}^{(n)}$. The derivation of the formulas parallels that given for the SRS energy [24]; it is given elsewhere [25]. The SRS derivation combined Eq. (1) with the commutator identity $\left[\hat{H}^\circ + \hat{V}, \hat{\mathscr{A}}\right] = 0$, the cPA theory derivation combines Eq. (3) with $\hat{\mathscr{A}}\left(\hat{H}^\circ + \hat{\mathscr{V}}\right) - \left(\hat{H}^\circ + \hat{\mathscr{V}}^\dagger\right)\hat{\mathscr{A}} = 0$. The cPA analog of the SRS energy (Eq. 2) is

$$\Delta E_{\mathrm{S}}(\lambda) = \langle F^\circ|(\hat{\mathscr{V}}^\dagger + D)\hat{\mathscr{A}}|F(\lambda)\rangle / \langle F^\circ|\hat{\mathscr{A}}|F(\lambda)\rangle, \tag{11}$$

the corrected SRS (cSRS) energy. It differs from the SRS expression (Eq. 2) not only in $\hat{\mathscr{V}}^\dagger + D$ replacing $\hat{V}$ and F (λ) from (Eq. 10) replacing the PA F (λ), but also in the omission of the multiplicative factor, λ. In deriving Eq. (11) we discarded the term $(1 - \lambda)\langle F^\circ|\hat{\mathscr{A}}\hat{\mathscr{V}}|F(\lambda)\rangle$ because it contributes nothing in the $\lambda = 1$ limit. In so doing, we discarded contributions of all orders in λ.

The arguments leading to Eq. (11) are repeated to obtain the improved energy

$$\Delta E_{\mathrm{I}}(\lambda) = \frac{\left(\mathscr{E}^{(1)} + D\right)\left\langle F^\circ\middle|\hat{\mathscr{A}}\middle|F(\lambda)\right\rangle + \langle F^{(1)}|(\hat{\mathscr{V}}^\dagger + D)\hat{\mathscr{A}}|F(\lambda)\rangle}{\left\langle F^\circ + F^{(1)}\middle|\hat{\mathscr{A}}\middle|F(\lambda)\right\rangle} . \tag{12}$$

Substitution of the PA functions and energies, replacing $\hat{\mathscr{V}}^\dagger$ by $\hat{V}$, and setting $D = 0$, gives the improved SRS (IRS) energy [24]. It is generally more accurate than the SRS formula [24]. Results calculated with Eq. (12) using the cPA F (λ) and $\mathscr{E}^{(1)}$ are corrected IRS (cIRS) energies.

We applied the cPA theory to the lowest states of $\mathrm{He_2}$ and $\mathrm{HeLi^+}$ and to the lowest triplet and singlet states of LiH. We present results here only for singlet LiH, the system which offers the greatest challenge. It forms a covalent bond; the others do not. It has an infinite number of unphysical energies below the ground-state energy; $\mathrm{He_2}$ and $\mathrm{HeLi^+}$ have only two. The SRS energies for singlet LiH, compared to the energies of the other systems, are very inaccurate around R_{e}.

The calculations were done using a program which differs from those previously described [8, 18] primarily in the theory implemented. The program transforms the operator equations into matrix equations in a full configuration interaction (FCI) approximation. It is not an implementation meant for practical use, but one that allows us to study SAPTs without introducing approximations beyond those of the perturbation theory and the use of finite basis sets. In effect, our calculations are done on numerically solvable, realistic models of real molecules. We used set 3 of the LiH basis sets used previously [18]. It gives 9,728 configurations. We set $c_{\mathrm{Li}} = 2.0$ bohr and $c_{\mathrm{H}} = 0$.

We summarize the results obtained for singlet LiH by substituting F° and the first-order functions and energies of the PA and cPA theories in Eqs. (11) and (12) in Fig. 1. Each curve represents the perturbation theory interaction energy divided by the FCI energy. The closer the ratio is to 1, the more accurate the perturbation theory energy. The cSRS energies are perceptibly more accurate than the SRS results only for $R < 5$ bohr, but the improvement is small relative to the SRS error. The same is true for the cIRS and IRS energies. At the largest R values, the perturbation theories are almost exact because they reproduce exactly the leading terms in the asymptotic $1/R$ expansion. In contrast, substituting the AM theory $F^{(1)}$ and $\mathscr{E}^{(1)}$ in Eq. (11) gives less than half of the asymptotic energy; in Eq. (12) less than three-fourths [22]. The very large errors shown at the smallest R values are misleading. It is not so much that the perturbation theory energies become less accurate there but that the FCI energy rapidly increases to zero.

The results obtained for HeLi$^+$ are like those for LiH except that the cSRS energy is less accurate than the SRS energy for $R < 5$ bohr and the IRS energy is less accurate than the SRS energy for $R < 4$ bohr. The calculations on He$_2$ and triplet LiH revealed no significant difference between the cSRS and SRS energies and between the cIRS and IRS energies. For the latter two systems, R_{e} is much greater than the largest c, namely, for He$_2$ $R_{\mathrm{e}} > 25c_{\mathrm{He}}$ and for triplet LiH $R_{\mathrm{e}} > 5c_{\mathrm{Li}}$. In contrast, $R_{\mathrm{e}} \cong 1.5c_{\mathrm{Li}}$ for singlet LiH and $R_{\mathrm{e}} \cong 2.4c_{\mathrm{Li^+}}$ for HeLi$^+$.

It may seem disappointing that the cPA and SRS theories yield equivalent numerical results, but numerical accuracy is not the SRS theory's major shortcoming. It is that carried to infinite order the SRS theory cannot predict even ground-state energies for most systems because $\mathscr{E}^{\circ}$ and E_1 are on different sheets of $\mathscr{E}(\lambda)$ [8]. The cPA eigenproblem (Eq. 3), by design, has no unphysical eigenvalues below the physical ground-state solution. The physical solution's eigenvalue E_1–D lies on the same sheet of the $\mathscr{E}(\lambda)$ surface as $\mathscr{E}^{\circ}$, a necessary condition for convergence of the perturbation expansion.

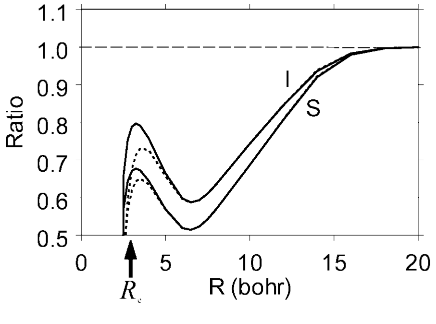

Fig. 1. Comparison of the accuracy of the singlet ground-state interaction energy between Li and H calculated with the perturbation theories described in Sects. 1 and 3. Each curve represents the ratio of a perturbation theory interaction energy to the full configuration interaction (*FCI*) energy. The *lower pair of curves*, labeled *S*, compare the symmetrized Rayleigh–Schrödinger (*SRS*) energy ratio (*dotted line*) to the corrected SRS (*cSRS*) energy ratio (*solid line*). They differ noticeably only for $R < 5$ bohr. The *upper pair of curves*, labeled *I*, compare the improved SRS (*IRS*) energy ratio (*dotted line*) to the corrected IRS (*cIRS*) energy ratio (*solid line*). The SRS and IRS energies were calculated using the first-order polarization approximation (*PA*) function and energy; the cSRS and cIRS were calculated using the first-order corrected PA function and energy

4 Zero-order induction

From a practical perspective it is most desirable that high accuracy be achieved by an SAPT at first order in the wave function. In this section we show that an alternative choice for the unperturbed problem markedly improves the accuracy achieved around the potential minimum while matching the high accuracy of the SRS and cPA theories at the largest separations. The arguments that suggest the alternative choice will be given in a later, detailed account of the theory.

Because at infinite separation the eigenfunction F_1 of Eq. (3) becomes equal to F° it is reasonable to assume that F_1 can be accurately approximated at large R by a function χ_{A} of the A coordinates times a function χ_{B} of the B coordinates. It is also reasonable that χ_{A} and χ_{B} are eigenfunctions of Hamiltonians for each atom in the field of the other. Examination of the induction contribution to the first-order cPA function suggests that χ_{A} should be an eigenfunction of

$$\hat{H}_{\mathrm{A}} = \hat{H}^{\circ}_{\mathrm{A}} + \hat{v}^{\mathrm{B}}_{\mathrm{A}} + \hat{J}^{\mathrm{B}\circ}_{\mathrm{A}} - (1-w)\hat{u}^{\mathrm{B}}_{\mathrm{A}} \ , \tag{13}$$

where $\hat{H}^{\circ}_{\mathrm{A}}$ is the unperturbed A-atom Hamiltonian, $\hat{J}^{\mathrm{B}\circ}_{\mathrm{A}}$ is Coulomb potential calculated using the lowest eigenfunction of $\hat{H}^{\circ}_{\mathrm{B}}$, and $w = N_{\mathrm{A}}!N_{\mathrm{B}}!N!$. The factor w is the weight of the identity operator in $\hat{\mathscr{A}}$. The calculation of an eigenfunction of $\hat{H}_{\mathrm{A}}$ is comparable in difficulty to calculating an eigenfunction of $\hat{H}^{\circ}_{\mathrm{A}}$.

Equation (3) is the starting point for the second new SAPT. We choose

$$\hat{H}^{(0)} = \hat{H}_{\mathrm{A}} + \hat{H}_{\mathrm{B}} \tag{14}$$

as the unperturbed Hamiltonian rather than $\hat{H}^{\circ}$. The unperturbed eigenfunction $F^{(0)} = \chi_{\mathrm{A}}\chi_{\mathrm{B}}$, the product of the lowest eigenfunctions of $\hat{H}_{\mathrm{A}}$ and $\hat{H}_{\mathrm{B}}$. Its eigenvalue $E^{(0)}$ is the sum of the lowest $\hat{H}_{\mathrm{A}}$ and $\hat{H}_{\mathrm{B}}$ eigenvalues. It follows from Eq. (3) that the perturbation is

$$\hat{\mathscr{V}} = \hat{g} - \hat{J}^{\mathrm{B}\circ}_{\mathrm{A}} - \hat{J}^{\mathrm{A}\circ}_{\mathrm{B}} + \hat{\mathscr{A}}(\hat{u} - D) - w\hat{u} \ . \tag{15}$$

To linearize Eq. (3) we set $D = \langle F^{(0)} | \hat{\mathscr{A}}\hat{u} | F^{(0)} \rangle / \langle F^{(0)} | \hat{\mathscr{A}} | F^{(0)} \rangle$. We make the usual assumptions: $\mathscr{E}(\lambda) = \mathscr{E}^{(0)} + \sum_{n=1}^{\infty} \lambda^n \mathscr{E}^{(n)}$ and $F(\lambda) = F^{(0)} + \sum_{n=1}^{\infty} \lambda^n F^{(n)}$, with $\langle F^{(0)} | F^{(0)} \rangle = 1$ and $\langle F^{\circ} | F(\lambda) \rangle = 1$. The set of perturbation equations follows from

$$\left(\hat{H}^{(0)} + \lambda\hat{\mathscr{V}}\right)F(\lambda) = \mathscr{E}(\lambda)F(\lambda) \ . \tag{16}$$

Because the zero-order function $F^{(0)}$ includes induction corrections to F° we call this the zero-order induction (ZI) theory. The ZI interaction energy is calculated from Eqs. (11) and (12) by substituting the ZI functions and energies for the cPA, then adding $\mathscr{E}^{(0)} - E^{\circ}$.

We applied the ZI theory to the systems on which the cPA theory was tested but we report here only the results obtained for the most difficult case, singlet LiH. We present in Fig. 2 results calculated with the energy Eqs. (11) and (12). The PA calculations were described in Sect. 3. The ZI results were calculated by substituting the ZI function $F^{(0)} + F^{(1)}$ for $F(\lambda)$, $F^{(0)}$ for F° and the ZI $\mathscr{E}^{(1)}$ in Eqs. (11) and (12). We used the definitions of $\hat{\mathscr{V}}$ and D given in this section. All the calculations used $c_{\mathrm{Li}} = 2.0$ bohr. The results obtained with Eq. (11) are labeled SZI, and those obtained with Eq. (12) are labeled IZI.

Figure 2 shows that the ZI theory is more accurate than the SRS theory at all R and greatly so around $R_e \cong 3.0$ bohr. Both theories become exact, ratio equal to 1, at the largest R values. At R_e the SZI energy is in error by 2.4% and the IZI energy by 1.1%. The ZI theory is least accurate at $R = 7.0$ bohr, where the SZI error is 23.6% and the IZI error is 22.4%. Attempts to improve the accuracy there by defining $\phi\ (r)$ differently gave no significant improvement. By carrying the ZI calculations to third order in the wave function the error was cut in half.

Figure 2 raises the question, how can the ZI theory be so accurate around R_e and at large R, but so poor at intermediate distances? The answer is that by including induction contributions in the zero-order function the ZI theory improves the cPA theory most at smaller R. At the largest R values the interaction energy is given accurately by the asymptotic dispersion energy, which the first-order cPA and ZI functions reproduce correctly. It may seem surprising that the induction contribution is so important around R_e but the same effect has been noted in calculations on ground-state H_2 [26].

An alternative view of the accuracy of the ZI theory is provided by Fig. 3. We remarked previously that plotting the ratio of the approximate interaction energies to the FCI energy could be misleading with regard to the significance of the errors. In Fig. 3 the SRS and IZI interaction energies are compared directly to the FCI values.

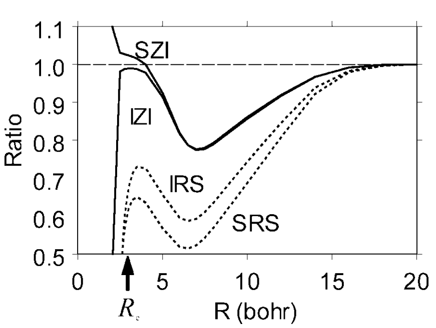

Fig. 2. Comparison of the accuracy of the singlet ground-state interaction energy between Li and H calculated with the perturbation theories described in Sects. 1 and 4. Each curve represents the ratio of a perturbation theory energy to the FCI interaction energy. The SRS and IRS energies were calculated using the PA theory's first-order wave function and energy. The zero-order induction (*ZI*) energies obtained with Eq. (11) (*SZI*) and those obtained with Eq. (12) (*IZI*) were calculated using the ZI theory's zero- and first-order wave functions and its first-order energy

5 Discussion

We have outlined two new SAPTs and shown how they are better than the SRS theory. A detailed exposition of the theories and the results obtained with them will be given elsewhere.

We have designed the new SAPTs with three goals in mind. The first is the traditional goal that the product of unperturbed atomic wave functions be an exact solution of the starting eigenproblem at infinite separation. The second goal, one not achieved by the EL-HAV and AM-AP theories, is that the correct asymptotic dependence on $1/R$ be calculable from the first-order wave function. Lastly, that carried to infinite order the theories should be capable, at least in principle, of giving the physical ground-state energy. The PA/SRS theory clearly fails in this regard for nearly all systems [8]. There is good reason to believe that the HS theory also fails [18, 19]. The new theories achieve all three goals.

To achieve simultaneously the second and third goals we introduced the short-range potential $\hat{u} = \hat{u}_{\mathrm{B}}^{\mathrm{A}} + \hat{u}_{\mathrm{A}}^{\mathrm{B}}$. The potential $\hat{u}_{\mathrm{B}}^{\mathrm{A}}$ inhibits the transfer of valence electrons from atom B to atom A and thus prevents the collapse of the B electrons into the A-atom core. We made $\hat{u}_{\mathrm{B}}^{\mathrm{A}}$ short-ranged so it could not affect the asymptotic $1/R$ dependence of the interaction energy. The potential $\hat{u}_{\mathrm{B}}^{\mathrm{A}}$ depends on a parameter c_{A} characteristic of A. The effect of $\hat{u}$ is to shift the lowest unphysical energy $\mathscr{E}_1^{\mathrm{u}}$ sufficiently far above the physical ground-state energy, E_1, to make $\mathscr{E}_1^{\mathrm{u}} > E_1 - D$. The perturbation calculations show that the asymptotic properties of both the cPA and ZI $F^{(1)}$s are as desired. By solving Eq. (7) we verified that $\mathscr{E}_1^{\mathrm{u}} > E_1 - D$ from R a little less than R_e to infinity with the c parameters chosen as suggested. This means

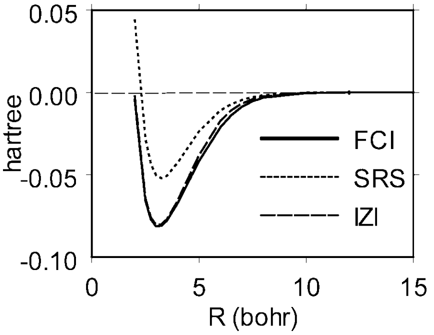

Fig. 3. Direct comparison of the SRS and IZI interaction energies, truncated after first order in the wave function, for the $^1\sum$ ground state of LiH to the FCI energy at a range of separations R

that $\mathscr{E}^\circ$ and E_1–D are on the same sheet of the Riemann surface; a necessary condition for convergence of the perturbation expansion to the physical ground-state solution.

Herring introduced formally a potential akin to $\hat{u}_{\mathrm{B}}^{\mathrm{A}}$ as a means of obtaining atomic-like functions to use in understanding the spin Hamiltonian at large separations [23]. In effect, he worked with approximate eigenfunctions of $\hat{H}^\bullet = \hat{H}^\circ + \hat{V} - \hat{u}$. He showed that $\hat{u}$ in $\hat{H}^\bullet$ made its lowest-energy solution localize the A electrons about the A nucleus and the B electrons about the B nucleus and that it became equal to F° at infinite separation. The terms we added to $\hat{H}^\bullet$ to get Eq. (3) ensure that $\hat{\mathscr{A}}F_1 \propto \Phi_1$, the physical ground-state function [21, 22]. The terms added also assure that the lowest eigenfunction of Eq. (3) is least distorted from that of $\hat{H}^\bullet$ and, thus, that it localizes, as much as possible, each atom's electrons about its nucleus. In the $R = \infty$ limit, $\mathscr{E}^\circ$ is a nondegenerate eigenvalue of Eq. (3), whereas it is a degenerate eigenvalue of $\hat{H}^\circ + \hat{V}$, i.e., Eq. (3) exhibits no exchange degeneracy. This should make the radius of convergence of perturbation theories based on Eq. (3) larger than those based on Eq. (1).

Patkowski, Jeziorski and Szalewicz (PJS) carried out calculations on H_2 [20] and LiH to study the effect on convergence of a short-range potential incorporated into several SAPT variants, recommending in the end a regularized EL-HAV theory. The PJS short-range potential, $\hat{V}_{\mathrm{t}}$ differs from our $\hat{u}$ only in that $\phi\ (r) = r^{-1}\exp\ (-\eta r^2)$ rather than the function in Eq. (9). To facilitate comparison to our work we note that the two forms of regularized EL-HAV theory tested correspond to solving, in our notation,

$$\left(\hat{H}^\circ - \mathscr{E}^\circ + \hat{V} - \hat{u} + \hat{u}\hat{\mathscr{A}}\right)F = (\mathscr{E} - \mathscr{E}^\circ)\hat{\mathscr{A}}F \ . \tag{17}$$

This should be compared to our Eq. (3). The most significant differences are that $\hat{\mathscr{A}}F$ appears on the right rather than just F and that $\hat{u}\hat{\mathscr{A}}$ appears on the left rather than $\hat{\mathscr{A}}\hat{u}$. A physical eigenfunction Φ_{k} of $\hat{H}^\circ + \hat{V}$, substituted for F, satisfies Eq. (17) but not Eq. (3). The Φ_{k} are, however, eigenfunctions of the Hermitian adjoint of the operator in square brackets in Eq. (3). The PJS results suggest what we expect to find with the cPA and ZI theories. They found that introducing $\hat{u}$ increased the radius of convergence of the SAPTs and that the contribution of $\hat{u}\hat{\mathscr{A}}$ to F was relatively unimportant for calculating the interaction energy. The last result is consistent with our results with the cPA theory.

The primary difference between the derivations of the cPA and PA/SRS theories is that the former starts from Eq. (3), the latter from Eq. (1). They both use $\hat{H}^\circ$ as the unperturbed Hamiltonian. The most important difference between the properties of Eqs. (1) and (3) lies in their energy spectra. The lowest unphysical energy, $\mathscr{E}_1^{\mathrm{u}}$, of Eq. (3) was made to be greater than the lowest physical energy, $\mathscr{E}_1 = E_1 - D$. The lowest physical energy of eq. (1) generally lies in a continuum of unphysical energies. The most important consequence of this difference is that the cPA theory can give uniquely the physical ground-state energy, E_1, if carried to infinite order; the PA/SRS theory cannot [8]. The equations for the cPA perturbation functions and energies differ from the PA/SRS equations only through the terms $-\hat{u} + \hat{\mathscr{A}}(\hat{u} - D)$ in the former. The effect of these terms on the interaction energy is small in the lowest orders, thus explaining why the PA/SRS theory works well enough when truncated to low order.

Because the cPA theory was no more accurate than the PA theory when the wave function was truncated after first order we developed the ZI theory. We started from Eq. (3) again, but we did not set the unperturbed Hamiltonian $\hat{H}^{(0)}$ equal to $\hat{H}^\circ$. We defined it instead, Eqs. (13) and (14), so that $F^{(0)}$ would be a product of polarized atomic functions, functions which include changes induced in each atom by its neighbor. The results for LiH show that the ZI theory is much more accurate than the cPA and SRS theories around R_{e}. The price one pays for this is that one must approximate $F^{(0)}$ as well as F°, and the difference $\mathscr{E}^{(0)} - \mathscr{E}^\circ$. The latter may be calculated directly.

We have shown that one can design fundamentally sound SAPTs by understanding the cause of the fundamental problems of the PA/SRS theory and by introducing changes in the traditional approach to counteract the cause. We have shown that this can be done in a way that exploits our understanding of the separated atom limit and equals the ability of the PA/SRS theory to reproduce correctly the asymptotic $1/R$ dependence of the energy in low order.

Acknowledgements. I have benefited from questions and comments on the preliminary reports of this work at the 1996 American Conference on Theoretical Chemistry and at the 1997 and 2001 Sanibel Symposia. In particular I am grateful to Bogumil Jeziorski for his comments on my 1996 poster and this manuscript, and for preprints of his recent work. I thank Sam Trickey for his question at the 1997 Sanibel Symposium concerning the accuracy of the ZI theory at intermediate separations.

Note added in proof

At the end of Sec. 2 we stated that there was no upper bound to the parameter c. In a private communication B. Jeziorski has pointed out that one can place an upper bound on c by considering the states that arise from the transfer of electrons between A and B when $\lambda = -1$. The larger c, the lower their energies, which is just the opposite of the behaviour of such states at $\lambda = +1$. This point will be considered at length in the full paper on the cPA/cSRS theory.

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