

Convergence Properties of the Intermolecular Force Series (1/R-Expansion)

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It is proven that the total energy of interacting molecular systems A and B at large intermolecular distances R can be expanded in a semi-convergent series in powers of $1/R$. It is further proven that "exchange forces" vanish faster than any power of $1/R$.

Key words: Long range forces – Intermolecular interactions – $1/R$ -expansion – Exchange forces

1. Introduction

It appears to be generally accepted that the intermolecular force series ($1/R$ -expansion) of the interaction energy between two molecules A and B

$$\Delta E(R) = E_{AB}(R) - (E_A + E_B) = \sum_{v=0}^{\infty} E_v R^{-v} \quad (1)$$

is a semiconvergent series [1]. This means that the following relationships hold although the series occurring in (1) may diverge for all R

$$\lim_{R \rightarrow \infty} R^N \left[\Delta E(R) - \sum_{v=0}^N E_v R^{-v} \right] = 0 \quad (2)$$

or, equivalently

$$\Delta E(R) = \sum_{v=0}^N E_v R^{-v} + O(R^{-N-1}). \quad (3)$$

In this context one often refers to a paper of Brooks [2], who did not give a rigorous proof for the semiconvergence of the $1/R$ -expansion, however. In his considerations, Brooks has tacitly assumed that the exact wavefunction may be expanded in powers of $1/R$ (otherwise the quantity $E'_N(R)$ defined in Eq.(21) of Ref. [2] is not a power series in $1/R$) and has explicitly assumed that the exact wavefunction for the supersystem AB vanishes exponentially in the region of the configuration space where the multipole expansion of the interaction potential diverges. Besides these two assumptions, which will essentially be justified in this paper, Brooks has disregarded the antisymmetry of the exact wavefunction and Eq.(23) of Ref. [2] is not correct in general as will be shown in the appendix.

A rigorous proof for the semiconvergence of (1) has so far only been given

by Coulson [3] for the polarization expansion of the H_2^+ system. The proof of Coulson is based on the explicit form of the eigenfunctions of the hydrogen atom and consequently cannot be generalized to n -electron atoms ($n > 1$) or to molecules where the exact wavefunctions are not known.

An instructive discussion of the semiconvergence of the $1/R$ -expansion has been given by Dalgarno and Lynn [4] for the second order long range force of the H_2^+ system.

In the present work we give a rigorous proof for the semiconvergence of the $1/R$ -expansion for the interaction energy $\Delta E(R)$ in the Born-Oppenheimer approximation and neglecting relativistic effects. The proof consists essentially of two steps. We first consider the $1/R$ -expansion of the interaction potential and show that the perturbation corrections to the wavefunction (in the Rayleigh-Schrödinger perturbation expansion with $1/R$ as perturbation parameter) vanish faster than q_i^{-n} for arbitrary n , where q_i is an arbitrary Cartesian coordinate of an electron from A or B. It is then almost trivial to show that the $1/R$ -expansion for the wavefunction and energy are asymptotic or semiconvergent approximations to the exact quantities.

We further show that the so called "exchange terms" vanish faster than any power of $1/R$.

2. Properties of the $1/R$ -Expansion

We consider the interaction between two molecules A and B. Let us denote the nuclear charges, nuclear and electronic coordinates of A by Z_α , R_α , r_i , and the corresponding quantities of system B by Z_β , S_β , s_k . The vectors are defined with respect to the centers of A and B – the definition of which is, of course, arbitrary – which are separated by R , where $R = |R|$. We then decompose the total Hamiltonian H in the usual way.

$$H = H_0 + V \quad (4)$$

$$H_0 = H_A + H_B \quad (5)$$

$$H_A = - \sum_i \left[\frac{\Delta_i}{2} + \sum_\alpha Z_\alpha |r_i - R_\alpha|^{-1} \right] + \sum_{i < j} |r_i - r_j|^{-1} \quad (6)$$

$$H_B = - \sum_k \left[\frac{\Delta_k}{2} + \sum_\beta Z_\beta |s_k - S_\beta|^{-1} \right] + \sum_{k < l} |s_k - s_l|^{-1} \quad (7)$$

$$V = - \sum_{k, \alpha} Z_\alpha |R_\alpha - R - s_k|^{-1} - \sum_{i, \beta} Z_\beta |R + S_\beta - r_i|^{-1} + \sum_{i, k} |r_i - R - s_k|^{-1} \quad (8)$$

The multipole expansion of V will be written in the form [5]

$$V' = \sum_{v=1}^{\infty} R^{-v} Q_v(r, s) \quad (9)$$

where the Q_v are homogenous polynomials of degree $(v-1)$. The expansion (9)

converges uniformly if

$$\begin{aligned} |r_i| &\leq M \\ |R_\alpha| &\leq M \\ |s_k| &\leq M \\ |S_\beta| &\leq M \end{aligned} \quad (10)$$

for arbitrary

$$M < R/2 \quad (11)$$

If we define

$$V'_N = \sum_{v=1}^N R^{-v} Q_v \quad (12)$$

we can write

$$V = V'_N + O(R^{-N-1}) \quad (13)$$

in any region of configuration space for which (10) and (11) hold.

We now consider the Rayleigh-Schrödinger perturbation expansion (with $1/R$ as perturbation parameter) for the eigenfunction and eigenvalue of the Hamiltonian H'

$$H' = H_0 + \sum_{v=1}^{\infty} R^{-v} Q_v \quad (14)$$

$$(H' - E')\Psi' = 0 \quad (15)$$

$$E' = \sum_v E_v R^{-v} \quad (16)$$

$$\psi' = \sum_v R^{-v} \psi_v \quad (17)$$

where ψ_v and E_v are obtained from the equations of Rayleigh-Schrödinger perturbation theory

$$(H_0 - E_0)\psi_v = - \sum_{\mu=0}^v (Q_\mu - E_\mu)\psi_{v-\mu} \quad (18)$$

with the zero order equations

$$\psi_0 = \psi_A \cdot \psi_B \quad (19)$$

$$E_0 = E_A + E_B \quad (20)$$

$$(H_A - E_A)\psi_A = 0 \quad (21a)$$

$$(H_B - E_B)\psi_B = 0 \quad (21b)$$

It should be noted that H_0 and H' commute with permutations of electrons within system A or B, but not with permutations which interchange electrons from A and B.

We further point out that the subsequent considerations remain valid for the treatment of interacting identical systems ($A=B$) if the systems are in different states ψ_A and ψ'_A . In such a resonance case we have to replace ψ_0 as given in Eq.(19) by

$$\psi_0 = \psi_A \psi'_A \pm \psi'_A \psi_A \quad (19a)$$

which does not affect our conclusions, however.

As the perturbation operators Q_ν are not bounded with respect to H_0 , compare the discussion of the Stark effect in [6], we have to show first that ψ_ν and E_ν exist at all in the sense of Hilbert space theory. The problem here is that the r.h.s. of Eq.(18) might not be well defined in Hilbert space. In order to exclude this possibility we have to show that $Q_\nu \psi_\mu$ is square integrable for arbitrary ν and μ .

For this purpose we prove the following theorem.

Let q_k denote an arbitrary Cartesian coordinate of an electron in system A or B. (x, y, z component of r_i or s_k) If the Hilbert space vector $f \in \mathcal{H}$ is in the domain of q_k^n for all $n > 0$

$$\|q_k^n f\| < \infty, \quad n = 1, 2, 3, \dots \quad (22)$$

it follows that the solution φ of

$$(H_0 - E_0)\varphi = f \quad (23)$$

is also in the domain of q_k^n

$$\|q_k^n \varphi\| < \infty, \quad n = 1, 2, 3, \dots \quad (24)$$

provided E_0 is an isolated eigenvalue of H_0 .

Proof. The solution φ of (23) is determined only up to an arbitrary solution of the homogeneous equation

$$(H_0 - E_0)\varphi_0 = 0 \quad (25)$$

Since the bound state eigenfunctions of H_A and H_B decay exponentially [7–9], it follows that any solution φ_0 of (25) (which is a finite dimensional linear combination of products of eigenfunctions of H_A and H_B) vanishes also exponentially. This holds only if E_0 is an isolated eigenvalue of H_0 , i.e. is not a point in the continuous spectrum. If P_0 denotes the projection operator onto the linear space of solutions of (25), Eq.(23) may then be written as

$$(1 - P_0)\varphi = \frac{1 - P_0}{H_0 - E_0} f. \quad (26)$$

Let us assume for the moment that we are allowed to use the formal commutation rule

$$[q_k^n, H_0] = -[q_k^n, \frac{1}{2}A_k] = -\frac{1}{2}n(n-1)q_k^{n-2} + n\frac{\partial}{\partial q_k}q_k^{n-1} \quad (27)$$

From (23) – compare also (26) – we then get an explicit representation of $q_k^n \varphi$

$$(1 - P_0) q_k^n \varphi = \frac{1 - P_0}{H_0 - E_0} \left[q_k^n f - \frac{1}{2} n(n-1) q_k^{n-2} \varphi + n \frac{\partial}{\partial q_k} q_k^{n-1} \varphi \right] \quad (28)$$

Since E_0 is by assumption on isolated eigenvalue of H_0 , the operators $(H_0 - E_0)^{-1} (1 - P_0)$ and $(H_0 - E_0)^{-1} (1 - P_0) \frac{\partial}{\partial q_k}$ are bounded operators (note that $\frac{\partial}{\partial q_k}$ is H_0 bounded [10]). This means that the r.h.s. of (28) is well defined for $n=1$ and the above theorem follows from a simple recurrence procedure.

The justification for the use of the commutation rule (27) is identical to the one given by Combes [10] for the consideration of the eigenvalue equation of Schrödinger operators and need not be repeated here. *q.e.d.*

Let us now return to the perturbation equation (18). As the unperturbed wavefunction vanishes exponentially [7-9] and the Q_v are polynomials of degree $(v-1)$ in the q_k , it follows immediately from the theorem just proven that

$$\|q_k^n \varphi_1\| < \infty, \quad n = 1, 2, 3, \dots \quad (29)$$

and further, by recurrence

$$\|q_k^n \varphi_v\| < \infty, \quad v = 1, 2, \dots, \quad n = 1, 2, \dots \quad (30)$$

This establishes that the ψ_v and, hence, the E_v exist and are well defined in the sense of Hilbert space theory.

The remaining considerations are now quite simple and need not be justified in great detail. Since ψ_v and E_v are solutions of the perturbation equations (18), the partial sums

$$\psi'_N = \sum_{v=0}^N R^{-v} \psi_v \quad (31)$$

$$E'_N = \sum_{v=0}^N R^{-v} E_v \quad (32)$$

solve the Schrödinger equation (15) up to the order $(N+1)$

$$\|(H_0 + V'_N - E'_N) \psi'_N\| = O(R^{-N-1}) \quad (33)$$

where V'_N is defined in Eq.(12). Due to the asymptotic behaviour (30) of ψ_v and, hence, ψ'_N we furthermore have from Eq.(13)

$$\|(V - V'_N) \psi'_N\| = O(R^{-N-1}) \quad (34)$$

If we combine (33) and (34) we finally get

$$\|(H - E'_N) \psi'_N\| = O(R^{-N-1}) \quad (35)$$

This establishes, by means of the Weinstein criterion [11], that E'_N approximates an exact eigenvalue of H up to $O(R^{-N-1})$. The analogous statement for ψ'_N holds only if there is no other eigenvalue of H with the same $1/R$ -expansion. ψ'_N is in

general only an approximation (correct up to terms $O(R^{-N-1})$) to a linear combination of all those eigenfunctions of H which correspond to eigenvalues which have the same $1/R$ -expansion E'_N as found for ψ'_N .

3. Antisymmetry and Exchange Contributions

In dealing with electronic systems we are only interested in totally anti-symmetric wavefunctions. The wavefunctions obtained from a perturbation expansion with V or V' as perturbation, Eqs.(8, 9), are antisymmetric only with respect to a permutation of electrons within A or B but not with respect to an interchange between A and B. If n_A and n_B denote the number of electrons in A and B we can distribute the $n_A + n_B$ electrons in $\binom{n_A + n_B}{n_A}$ different ways on the subsystems A and B, and consequently obtain the same number of perturbed wavefunctions. These functions may be written as $P_{AB}\psi'_N$, where P_{AB} denotes the operator corresponding to a permutation which interchanges electrons from A and B. Since P_{AB} commutes with the total Hamiltonian H , it follows immediately from Eq.(35) that

$$\|(H - E'_N)P_{AB}\psi'_N\| = \|(H - E'_N)\psi'_N\| = O(R^{-N-1}) \quad (36)$$

which furthermore yields for any linear combination of the $P_{AB}\psi'_N$

$$\|(H - E'_N) \sum c(P_{AB})P_{AB}\psi'_N\| = O(R^{-N-1}) \quad (37)$$

The set of functions $P_{AB}\psi'_N$ is linearly independent and it is in fact an easy matter to conclude the following relationship from the asymptotic properties (30)

$$\lim_{R \rightarrow \infty} R^m \langle \psi'_N | P_{AB} \psi'_N \rangle = 0, \quad m > 0, \quad (38)$$

for arbitrarily large m .

In the case that ψ_A and ψ_B have spin (S_A, S_B) different from zero, we furthermore have $(2S_A + 1)(2S_B + 1)$ linearly independent functions (arising from the corresponding zeroth order functions) which fulfill Eq.(35) with the same E'_N .

We thus have a total of $\binom{n_A + n_B}{n_A} (2S_A + 1)(2S_B + 1)$ wavefunctions which span a representation of the permutation group. One may then construct the linear combinations which transform as the i th row of the irreducible representation Γ of the permutation group with spin quantum numbers S, m_S , by using the corresponding projection operators $\mathcal{O}(\Gamma, i, S, m_S)$. In analogy to (37) all these functions fulfill the following equation independent of Γ, i, S, m_S

$$\|(H - E'_N)\mathcal{O}(\Gamma, i, S, m_S)\psi'_N\| = O(R^{-N-1}) \quad (39)$$

We note that among the irreducible representations Γ of the permutation group which may occur here we certainly have the totally antisymmetric representation, but we also have other irreducible representations which are not admissible for a system of electrons.

If $\psi(S, m_S)$ denotes the exact electronic eigenfunction it furthermore follows

from Eq.(39) by means of the Weinstein criterion (Γ_a denotes the totally anti-symmetric representation of the permutation group)

$$\|\psi(S, m_S) - \mathcal{O}(\Gamma_a, S, m_S)\psi'_N\| = O(R^{-N-1}) \quad (40)$$

This results from the fact that – except for accidental degeneracy, which need not concern us here, and except for degenerate representations of the space group, which are easily dealt with – the irreducible representation specified by Γ_a and S occurs only once.

Eqs.(39) and (40) simply mean that exchange effects do not contribute to the $1/R$ expansion and must vanish faster than any power of $1/R$. We further note that the above discussion of exchange effects holds also if V itself is used as a perturbation instead of its multipole expansion V' .

4. Concluding Remarks

We have obtained the $1/R$ -expansion for the energy and the wavefunction in using the multipole expansion (12) even in those regions of configuration space where it diverges. This obviously indicates that the $1/R$ -expansion cannot converge (i.e. it has convergence radius zero), and the corresponding expansions for the energy and wavefunction are semiconvergent only. For the sake of completeness we may also give a direct proof of the divergence of the expansion (1) for the energy. Consider, as a simple example, the lowest singlet ($^1\Sigma_g^+$) and triplet state ($^3\Sigma_u^+$) of the H_2 molecule. Let us assume that (1) converges for $R > R_0$. Since the energies for the $^1\Sigma_g^+$ and $^3\Sigma_u^+$ states of H_2 have identical $1/R$ -expansion, as was proven at the end of the preceding section, this implies that the energies for the two states would be identical for $R > R_0$. This is certainly not the case which proves that our assumption about the convergence of the $1/R$ -expansion leads to a contradiction. The energy difference between the two states vanishes faster than any power of $1/R$, however, as follows from Eq.(39).

It has been shown by Claverie [12] that the Rayleigh-Schrödinger expansion with V as a perturbation does usually not converge (if it converges at all) towards a totally antisymmetric state if one starts from the electronic ground states of A and B. It has then been suggested by Claverie that using V or its $1/R$ -expansion as a perturbation might still be a reasonable procedure to compute long range forces if the interaction energies for the two states (the one to which the perturbation expansion converges and the electronic state one is interested in) differ by a function with sufficiently fast decrease. The considerations reported in this work give in fact a rigorous justification for this suggestion of Claverie.

Our treatment disproves the conjecture of Musher and Amos [13] that exchange terms are as important as the Coulombic terms ($1/R$ -expansion) for all R and that the sum of exchange terms “is, in all probability, infinite”. For this reason we cannot support the criticism of Musher and Amos with respect to the treatment of exchange forces by Herring and Flicker [14].

We finally note that the methods used in this study are easily extended to the treatment of three or more interacting systems. One has then to use the multipolar expansion of the interaction potential in terms of the intermolecular distances

R_{AB} , R_{BC} , R_{AC} etc., in order to prove that the interaction energy can be expanded in a semiconvergent series in R_{AB}^{-1} , R_{BC}^{-1} and R_{AC}^{-1} .

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Appendix

We want to comment briefly on Eq.(23) of Brooks' paper [2]

$$\langle \Phi | V - V'_N | \Phi \rangle = O(R^{-N-1}) \quad (A1)$$

where Φ denotes the exact wavefunction of the complex AB, V the interaction potential as defined in Eq.(8) and V'_N the $1/R$ -expansion of V up to terms in R^{-N} , see Eq.(12). Brooks' reasoning was essentially that (A1) is correct if integrated only over the region of configuration space where Eq.(9), converges and that the remaining volume integral gives exponentially decreasing contributions.

Due to the antisymmetry of Φ , Eq.(A1) cannot be correct. This is most easily verified if we consider the H_2 system as a simple example. If we associate - in the unperturbed system - electron 1 with nucleus a and electron 2 with b , we obtain for V , in an obvious notation

$$V = -\frac{1}{r_{a2}} - \frac{1}{r_{b1}} + \frac{1}{r_{12}} + \frac{1}{R} \quad (A2)$$

We may now replace the exact wavefunction Φ by the Heitler-London function Φ_{HL} (in its spinless form) which approximates Φ up to terms in R^{-3} .

$$\Phi_{HL} = [\varphi_a(1)\varphi_b(2) + \varphi_b(1)\varphi_a(2)] [2 + 2S^2]^{-\frac{1}{2}} \quad (A3)$$

$$S = \langle \varphi_a | \varphi_b \rangle \quad (A4)$$

We then get immediately

$$\langle \Phi_{HL} | V | \Phi_{HL} \rangle = -\langle \varphi_a | \frac{1}{r_{a1}} | \varphi_a \rangle (1 + S^2)^{-1} + O(\exp(-2R)) \quad (A5)$$

Since V'_N starts with a term in R^{-3} , we conclude that (A1) is not correct in general.

In the present treatment we have circumvented this kind of difficulty in using an equation like (A1) only for a wavefunction which was not antisymmetric, see Eq.(34). The antisymmetrization does not matter if we use the full Hamiltonian H , compare Eqs.(35-37), which has the full permutational invariance, whereas H_0 and V have not.

Note Added in Proof. After completion of this study a paper of R. H. Young, Intern. J. Quantum Chem. **9**, 47 (1975), came to our attention, where the divergence of the $1/R$ expansion is proven for the second order interaction energy (not the total interaction energy as in this work) between two hydrogen atoms. Young's comments on the paper of Brooks [2] are in part similar to those given in the introduction of this work. The present author is indebted to Dr. Laurinc for bringing Young's paper to his attention.

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