Generalized Heitler–London Theory for H₃: A Comparison of the Surface Integral Method with Perturbation Theory

Tanja I. Sachse
Max-Planck-Institut für Strömungsforschung, Bunsenstr.10, D-37073 Göttingen, Germany

Ulrich Kleinekathöfer
Institut für Physik, Technische Universität, D-09107 Chemnitz, Germany
(February 8, 2022)

Abstract

The generalized Heitler–London (GHL) theory provides a straightforward way to express the potential energy surface of H₃ in terms of Coulomb and exchange energies which can be calculated either by perturbation theory or using the surface integral method (SIM). By applying the Rayleigh–Schrödinger perturbation theory, GHL theory for the quartet spin state of H₃ is shown to yield results equivalent to the symmetrized Rayleigh–Schrödinger version of symmetry adapted perturbation theory (SAPT). This equivalence allows a comparison with the corresponding results obtained by the surface integral method. The surface integral result calculated with a product of atomic wave functions is found to have certain advantages over the perturbation approach.
I. INTRODUCTION

The generalized Heitler–London (GHL) theory provides a useful framework to calculate the potential energy surfaces for polyatomic systems\(^1\)\(^4\). Since the potential energy is expressed in terms of Coulomb and exchange energies it is possible to systematically separate out many–body effects in every single term contributing to the potential energy. In this paper some aspects of the three–body exchange effects occurring in \(H_3\) are examined in more detail.

Axilrod, Teller and Muto\(^5\) were the first to suggest a formula describing the leading long range three–body dispersion term for three spherically symmetric atoms. Since then the non–additive effects have been intensively studied and several review articles have been published\(^6\)\(^–\)\(^8\). In the GHL approach the potentials can be decomposed into Coulomb and exchange \textit{energies}, whereas in symmetry adapted perturbation theory (SAPT) these interactions are expressed in terms of Coulomb and exchange \textit{integrals} in the manner first introduced by Heitler and London. Recently, SAPT was formulated for the interactions of trimers\(^1\) and has been applied to numerical calculations up to third order for the quartet spin state of \(H_3\)\(^1\) and for the helium–trimer \(^1\) up to third order. Other three–body calculations for \(H_3\) are based on Heitler–London type calculations\(^1\)\(^2\)\(^–\)\(^4\)\(^15\)\(^–\)\(^17\). In the former the splitting into Coulomb and exchange part is as pointed out by the author himself not completely rigorous.

In a previous paper\(^3\) analytical results were reported for the doublet as well as for the quartet spin state for the \(H_3\) system based on the GHL theory. Two kinds of exchange energies appear: cyclic exchange energies, where all three electrons are involved, and two–body exchange energies in the presence of the respective third atom. The cyclic exchange energy of three hydrogen and three helium atoms\(^14\) was calculated using the surface integral method (SIM) which was previously applied to two atoms\(^1\)\(^2\)\(^–\)\(^4\)\(^15\)\(^–\)\(^17\). In a forthcoming paper\(^18\) it will be demonstrated that all exchange energies occurring in the \(H_3\)–system can be calculated either by the surface integral method or by using perturbation theory, and the corresponding results for the implicit three–body effect on the two–body exchange energies will be derived and compared.

For \(H_2\) it was previously shown that SAPT and GHL are equivalent\(^19\). The purpose of this paper is to compare the surface integral method calculations of the three–body effects in the exchange energies based on an atomic product wave function with the results of first to third order of SAPT which are only available for the quartet spin state of \(H_3\)\(^10\). In order to perform this comparison it is necessary to first prove that the SAPT and GHL theory expressions for the energy of the quartet state are equivalent. The results reveal that with the zeroth order wave function the surface integral result contains parts of the second order SAPT result and is therefore more efficient.

In Sections\(^11\) and\(^11\) the basic ideas of the GHL theory and polarization approximation are described. In Section\(^15\) the equivalence of the GHL and the symmetrized Rayleigh–Schrödinger (SRS) theories is demonstrated order by order. The latter is designated a weak symmetry forcing SAPT. Section\(^15\) reviews the surface integral method (SIM). Thereafter in Section\(^15\) the advantages of SIM over the perturbation approach will be demonstrated by comparing the numerical results of perturbation theory and SIM.
II. GENERALIZED HEITLER–LONDON THEORY FOR H₃

The application of generalized Heitler–London theory to H₃ was previously discussed in Ref. [3]. The generalized Heitler–London equation is given by

$$\hat{H}F = \sum g \epsilon_g \hat{T}(g)F$$  \hspace{1cm} (1)

where $F$ is the localized, i.e. non–symmetrized wave function, $\hat{T}(g)$ designates a permutation operator for the electron coordinates, and $\epsilon_g$ stands for the Coulomb ($g = I$) and exchange energies ($g \neq I$). Applying results from the theory of the symmetric group, the energy eigenvalues of the Hamiltonian can be derived. For the H₃–system, the result for the two doublet states is

$$\frac{1}{2} E_{GHL} = \epsilon_I - \epsilon_{123} \pm \sqrt{\frac{1}{2} \left[ (\epsilon_{12} - \epsilon_{23})^2 + (\epsilon_{23} - \epsilon_{13})^2 + (\epsilon_{13} - \epsilon_{12})^2 \right]}$$  \hspace{1cm} (2)

and for the quartet state

$$\frac{3}{2} E_{GHL} = \epsilon_I - \epsilon_{12} - \epsilon_{23} - \epsilon_{13} + 2\epsilon_{123}.$$  \hspace{1cm} (3)

The remainder of this paper will be concerned only with the quartet state.

III. POLARIZATION APPROXIMATION AND GENERALIZED HEITLER–LONDON (GHL) THEORY

The Born–Oppenheimer non–relativistic Hamiltonian of the three–body system is given by

$$\hat{H} = \hat{H}^0 + \hat{V}$$  \hspace{1cm} (4)

using

$$\hat{H}^0 = \hat{H}_A^0 + \hat{H}_B^0 + \hat{H}_C^0$$  \hspace{1cm} (5)

$$\hat{V} = \hat{V}_{AB} + \hat{V}_{BC} + \hat{V}_{AC}$$  \hspace{1cm} (6)

where $\hat{H}_A^0, \hat{H}_B^0$ and $\hat{H}_C^0$ are the Hamiltonians of three free hydrogen atoms and $\hat{V}_{AB}, \hat{V}_{BC}$ and $\hat{V}_{AC}$ describe the interaction between atoms A and B, B and C, as well as A and C, respectively. The polarization approximation [20] is based on the equation

$$\hat{H}F = E_p F$$  \hspace{1cm} (7)

where the polarization wave function $F$ and the polarization energy $E_p$ can be written as perturbation series

$$F = \sum \phi_n,$$  \hspace{1cm} (8)

$$E_p = \sum \epsilon_n.$$  \hspace{1cm} (9)
The zeroth order polarization wave function $\phi_0$ is the eigenfunction of the free Hamiltonian $\hat{H}^0$ and thus is a product of three free hydrogen wave functions. Starting from the GHL equation with $F$ chosen as the polarization wave function, Eq. (1) together with the Hamiltonian Eq. (4) can be written as

$$(\hat{H}^0 + \hat{V})(\sum_n \phi_n) = \sum_g \epsilon_g \hat{T}(g)(\sum_{n=0}^{N} \phi_n).$$ \hspace{1cm} (10)

Forming scalar products with $\hat{T}(g)\phi_0$ for each group element $g$

$$(\hat{T}(g)\phi_0, (\hat{H}^0 + \hat{V}) \sum_n \phi_n) = \sum_{g' \neq g} \epsilon_{g'} \hat{T}(g) \phi_0, \sum_{n=0}^{N} \hat{T}(g')\phi_n)$$ \hspace{1cm} (11)

a system of linear equations can be derived for the Coulomb energy $\epsilon_I$ as well as for the exchange energies $\epsilon_g (g \neq I)$ in terms of Coulomb integrals $J$, exchange integrals $K_g$, and overlap integrals $S_g$:

$$E_0 + J \approx \epsilon_I + \sum_{g' \neq g} \epsilon_{g'} S_{g'-1} : g = I$$

$$E_0 S_g + K_g \approx \epsilon_g + \sum_{g' \neq g} \epsilon_{g'} S_{g'-1,g} : g \neq I .$$ \hspace{1cm} (12)

The following notation for the $n$th order overlap, Coulomb and exchange integrals was used:

$$S_g := \sum_{n=0}^{M} S^n_g$$ \hspace{1cm} (13)

$$J := \sum_{n=0}^{M} J^n$$ \hspace{1cm} (14)

$$K_g := \sum_{n=1}^{M} K^n_g = \sum_{n=1}^{M} K^n_{g-1,g} ,$$ \hspace{1cm} (15)

where

$$S^n_g := (\hat{T}(g)\phi_0, \phi_n)$$ \hspace{1cm} (16)

$$J^n := (\phi_0, \hat{V}\phi_{n-1})$$ \hspace{1cm} (17)

$$J^0 = E_0$$ \hspace{1cm} (18)

$$K^n_g := (\phi_0, \hat{V}\hat{T}(g^{-1})\phi_{n-1}).$$ \hspace{1cm} (19)

The equalities $S^n_{g-1} = S^n_g$ and $K^{n-1}_{g} = K^n_g$ hold. In Ref. [18] it will be shown how the Coulomb and exchange energies can be expressed in terms of Coulomb, exchange and overlap integrals and how the order–by–order contributions to the Coulomb and exchange energies can be found.

The convergence properties of the polarization theory have been extensively discussed for the case of two hydrogen atoms [21]. For low orders it was shown that the perturbation series rapidly converges to the Coulomb energy [19, 21–23] though this is not the limit for the infinite order expansion. It is assumed that the behavior of this perturbation theory for a system of two atoms also roughly holds in the case of three atoms [9, 10]. Since here we are only interested in low orders, especially the first, this expected behavior justifies approximating the localized wave function via the polarization approximation for three hydrogen atoms as well.
IV. EQUIVALENCE OF THE GHL AND SRS THEORY FOR QUARTET H₃

In this section the order–by–order equivalence of the complete energy expressions obtained by using either the GHL or the SRS theory will be demonstrated. Both the GHL and SRS theories start with the Hamiltonian Eq. (3) and a zeroth order wave function which is a product of three free hydrogen atom wave functions. To demonstrate the equivalence of the first order expressions the first order SRS term will be expressed in terms of Coulomb and exchange energies. In Eq. (12) of Ref. [10] this term is given by

\[ \frac{3}{2} E_{SRS}^{1} = N_0 \left[ < \psi_0 | \hat{V} (1 - \hat{T}(12) - \hat{T}(23) - \hat{T}(13) + \hat{T}(123) + \hat{T}(132)) | \psi_0 > \right], \]  

(20)

which can be expressed with Eqs. (10) to (19) as

\[ \frac{3}{2} E_{SRS}^{1} = N_0 \left[ J^1 - K_{12}^1 - K_{23}^1 - K_{13}^1 + K_{123}^1 + K_{132}^1 \right], \]  

(21)

where

\[ N_0 = 1 - S_{12}^0 - S_{23}^0 - S_{13}^0 + S_{123}^0 + S_{132}^0. \]  

(22)

With Eq. (12) it is possible to express the first order contributions as

\[ J^1 = \epsilon_1^1 + \epsilon_{12}^1 S_{12}^0 + \epsilon_{23}^1 S_{23}^0 + \epsilon_{13}^1 S_{13}^0 + \epsilon_{123}^1 S_{123}^0 + \epsilon_{132}^1 S_{132}^0 \]  

(23)

\[ K_{12}^1 = \epsilon_{12}^1 + \epsilon_{1}^1 S_{12}^0 + \epsilon_{23}^1 S_{23}^0 + \epsilon_{13}^1 S_{13}^0 + \epsilon_{123}^1 S_{123}^0 + \epsilon_{132}^1 S_{132}^0 \]  

(24)

\[ K_{23}^1 = \epsilon_{23}^1 + \epsilon_{1}^1 S_{23}^0 + \epsilon_{12}^1 S_{123}^0 + \epsilon_{13}^1 S_{132}^0 + \epsilon_{123}^1 S_{123}^0 + \epsilon_{132}^1 S_{132}^0 \]  

(25)

\[ K_{13}^1 = \epsilon_{13}^1 + \epsilon_{1}^1 S_{13}^0 + \epsilon_{12}^1 S_{123}^0 + \epsilon_{23}^1 S_{23}^0 + \epsilon_{123}^1 S_{123}^0 + \epsilon_{132}^1 S_{132}^0 \]  

(26)

\[ K_{123}^1 = \epsilon_{123}^1 + \epsilon_{1}^1 S_{123}^0 + \epsilon_{12}^1 S_{123}^0 + \epsilon_{23}^1 S_{23}^0 + \epsilon_{13}^1 S_{132}^0 + \epsilon_{123}^1 S_{132}^0 \]  

(27)

\[ K_{132}^1 = \epsilon_{132}^1 + \epsilon_{1}^1 S_{132}^0 + \epsilon_{12}^1 S_{123}^0 + \epsilon_{23}^1 S_{23}^0 + \epsilon_{13}^1 S_{132}^0 + \epsilon_{123}^1 S_{132}^0 \]  

(28)

On inserting into Eq. (21) many terms cancel and Eq. (21) is equivalent to the first order contribution to Eq. (3)

\[ \frac{3}{2} E_{SRS}^{1} = N_0 \left[ J^1 - K_{12}^1 - K_{23}^1 - K_{13}^1 + K_{123}^1 + K_{132}^1 \right] = \epsilon_1^1 - \epsilon_{12}^1 - \epsilon_{23}^1 - \epsilon_{13}^1 + \epsilon_{123}^1 = \frac{3}{2} E_{GHL}^{1}. \]  

(29)

The rest of the proof will be done by complete induction. The claim of the induction is the equivalence of the GHL and SRS energy expressions up to nth order. From Eq. (12) of [10] the general nth–order expression for the interaction energy in SRS theory is found to be

\[ \frac{3}{2} E_{SRS}^{n} = N_0 \left[ < \psi_0 | \hat{V} (1 - \hat{T}(12) - \hat{T}(23) - \hat{T}(13) + \hat{T}(123) + \hat{T}(132)) | \psi_0^{(n-1)} > - \sum_{k=1}^{n-1} \frac{3}{2} E_{SRS}^{k} < \psi_0 | (1 - \hat{T}(12) - \hat{T}(23) - \hat{T}(13) + \hat{T}(123) + \hat{T}(132)) | \psi_0^{(n-k)} > \right] 

\[ = N_0 \left[ J^n - K_{12}^n - K_{23}^n - K_{13}^n + K_{123}^n + K_{132}^n \right] - \sum_{k=1}^{n-1} \frac{3}{2} E_{SRS}^{k} (-S_{12}^{n-k} - S_{23}^{n-k} - S_{13}^{n-k} + S_{123}^{n-k} + S_{132}^{n-k}) \]  

(30)

\[ \]
where \( N_0 \) is given by Eq. (23). Thus it is necessary to prove that

\[
\frac{3}{2} E_{GHL}^n = \epsilon_f^n - \epsilon_{12}^n - \epsilon_{23}^n - \epsilon_{13}^n + \epsilon_{123}^n + \epsilon_{132}^n
\]

\[
= \frac{3}{2} E_{SRS}^n .
\]

To perform a proof by induction it is necessary to show that also the \((n+1)\)st order terms of both theories are equal. To do so, the \((n+1)\)st order of GHL theory is expressed in terms of the quantities occurring in SRS theory. This can be achieved by inserting the solutions of both theories \([24]\) into the complete GHL energy for the \( \text{H}_3^- \)-quartet state \([24]\)

\[
\frac{3}{2} E_{GHL} = \epsilon_f - \epsilon_{12} - \epsilon_{23} - \epsilon_{13} + \epsilon_{123} + \epsilon_{132}
\]

\[
\approx \sum_{n=0}^{M} \frac{3}{2} E_{GHL}^n = \sum_{n=0}^{M} \left[ \epsilon_f^n - \epsilon_{12}^n - \epsilon_{23}^n - \epsilon_{13}^n + \epsilon_{123}^n + \epsilon_{132}^n \right]
\]

\[
= E_0 + \left[ J - K_{12} - K_{23} - K_{13} + K_{123} + K_{132} \right]^{-1}
\]

\[
\left[ 1 - S_{12} - S_{23} - S_{13} + S_{123} + S_{132} \right]
\]

\[
\sum_{n=0}^{M} \left[ J^n - K_{12}^n - K_{23}^n - K_{13}^n + K_{123}^n + K_{132}^n \right] .
\]

Collecting terms of \((n+1)\)st order leads to

\[
\frac{3}{2} E_{GHL}^{n+1} \left( 1 - S_{12}^0 - S_{23}^0 - S_{13}^0 + S_{123}^0 + S_{132}^0 \right)
\]

\[
= J^{n+1} - K_{12}^{n+1} - K_{23}^{n+1} - K_{13}^{n+1} + K_{123}^{n+1} + K_{132}^{n+1}
\]

\[
+ E_0 \left( -S_{12}^{n+1} - S_{23}^{n+1} - S_{13}^{n+1} + S_{123}^{n+1} + S_{132}^{n+1} \right)
\]

\[
- \sum_{k=0}^{n} \frac{3}{2} E_{GHL}^k \left( -S_{12}^{n+1-k} - S_{23}^{n+1-k} - S_{13}^{n+1-k} + S_{123}^{n+1-k} + S_{132}^{n+1-k} \right)
\]

\[
= N_0 \left[ J^{n+1} - K_{12}^{n+1} - K_{23}^{n+1} - K_{13}^{n+1} + K_{123}^{n+1} + K_{132}^{n+1}
\]

\[
- \sum_{k=1}^{n} E_{3/2}^{GHL,k} \left( -S_{12}^{n+1-k} - S_{23}^{n+1-k} - S_{13}^{n+1-k} + S_{123}^{n+1-k} + S_{132}^{n+1-k} \right) \right] .
\]

Using the claim of the proof, which stated that for all orders up to the \( n \)th the GHL term is equal to the SRS term, \( E_{3/2}^{GHL,k} \) in the last line can be replaced by \( \frac{3}{2} E_{SRS}^{(n+1)} \) for all orders \( 1, \ldots, n \). Thus Eq. (37) can be transformed into
\[ 3/2 E_{GHL}^{n+1} = N_0 \left[ J^{n+1} - K_{12}^{n+1} - K_{23}^{n+1} - K_{13}^{n+1} + K_{12}^{n+1} + K_{13}^{n+1} \right. \\
\left. - \sum_{k=1}^{n} \frac{3/2 E_{SRS}^k}{3/2 E_{SRS}} \left( -S_{12}^{n+1-k} - S_{23}^{n+1-k} - S_{13}^{n+1-k} + S_{12}^{n+1-k} + S_{13}^{n+1-k} \right) \right] \] 

(38)

and the equality also holds for the \((n+1)\)st order. Thus the contributions to the energy of the \(H_3\)–quartet state in the SRS and GHL theories are equal order by order.

One advantage of the GHL theory is that it permits the calculation of the exchange energies by other methods, such as the surface integral method. In Ref. [10], the non–additive energy terms of the quartet spin state of \(H_3\) have been calculated up to third order. The first order terms can be split into a polarization and an exchange part. Since the first order polarization energy is pairwise additive, the only non–additive term in first order is contained in the exchange term which in Eqs. (23) and (55) of Ref. [9] is given by

\[ E_{exch}^1(3, 3) = \psi_0 \left| \hat{V}_{AB} \left( \hat{T}(23) + \hat{T}(13) + \hat{T}(123) + \hat{T}(132) - S_{23}^0 - S_{13}^0 - S_{123}^0 - S_{132}^0 \right) \right| \psi_0 > \\
+ \psi_0 \left| \hat{V}_{AB} \left( \hat{T}(12) + \hat{T}(13) + \hat{T}(123) + \hat{T}(132) - S_{12}^0 - S_{13}^0 - S_{123}^0 - S_{132}^0 \right) \right| \psi_0 > \\
+ \psi_0 \left| \hat{V}_{AB} \left( \hat{T}(12) + \hat{T}(23) + \hat{T}(123) + \hat{T}(132) - S_{12}^0 - S_{23}^0 - S_{123}^0 - S_{132}^0 \right) \right| \psi_0 > , \] 

(40)

which can be expressed in terms of exchange energies as

\[ E_{exch}^1(3, 3) = \epsilon_{123}^1(1 - S_{123}^0) - \left[ \epsilon_{12}^1(1 + S_{12}^0) - \epsilon_{12}^{H_2,1}(1 + S_{12}^0) \right] \\
- \left[ \epsilon_{23}^1(1 + S_{23}^0) - \epsilon_{23}^{H_2,1}(1 + S_{23}^0) \right] - \left[ \epsilon_{13}^1(1 + S_{13}^0) - \epsilon_{13}^{H_2,1}(1 + S_{13}^0) \right] . \] 

(41)

This term is also obtained if the pure two–body contributions are subtracted from Eq. (29).

V. SURFACE INTEGRAL METHOD (SIM) FOR THE CALCULATION OF EXCHANGE ENERGIES

As shown in Refs. [14] and [18] all exchange energies occurring in the GHL–description of the \(H_3\) system, i.e. the two–body as well as the cyclic exchange energies, can be calculated by the surface integral method (SIM). The exchange energy \(\epsilon_{g_0} \) associated with the arbitrary group element \(g_0 \neq I \) is given accordingly by

\[ \epsilon_{g_0} = \left[ \int_V dv \left[ F^2 - (\hat{T}(g_0) F)^2 \right] \right]^{-1} \left[ \frac{1}{2} \int \sum \left\{ F \nabla \left[ \hat{T}(g_0) F - (\hat{T}(g) F) \right] \nabla F \right\} \cdot d\vec{s} \right. \\
- \sum_{g \neq I, g_0} \epsilon_g \int_V dv \left[ F(\hat{T}(g_0) F) - (\hat{T}(g) F)(\hat{T}(g) F) \right] . \] 

(42)

In order to compare numerical results for three–body exchange effects with the published SAPT results for \(H_3 \) [11], an expression for the non–additive exchange energy has to be obtained using SIM. The non–additive exchange energy basically contains the cyclic exchange
energy and the implicit three–body effects on the two–body exchange energies. As already pointed out in Ref. [14] it can be shown that for a choice of the partial volume \( V \) such that \( F \) is localized inside, all quantities occurring in the sum of Eq. (12) go to zero with at least a factor of \( e^{-R} \) faster than the surface integral itself if all internuclear distances are larger or equal to \( R \). This holds for all exchange energies. In a different paper [18] it will be shown how to find the implicit three–body effect from the complete surface integral expression for the two–body exchange energies. For product wave functions as used here the pure two–body part is given by the first line of formula Eq. (12), i.e. surface integral (SI) over denominator. The implicit three–body effect is contained in the second line of Eq. (12), i.e. the products of partial overlap integrals with exchange energies. Following the same scheme used in the Appendix of Ref. [14], these terms can be shown to asymptotically go to zero as \( e^{-5R} \) which is faster by a factor of \( e^{-3R} \) than the surface integral (SI) itself.

Using these results a GHL non–additive exchange energy for the quartet state of \( H_3 \) can be defined by simply subtracting the pure two–body contribution from the two–body exchange energies in the GHL result for the quartet state Eq. (3)

\[
\left(\frac{3}{2} E_{GHL}^{exch}\right)_{\text{third}} = 2\epsilon_{123} - \left[\epsilon_{12} - \epsilon_{12}^{H2}\right] - \left[\epsilon_{23} - \epsilon_{23}^{H2}\right] - \left[\epsilon_{13} - \epsilon_{13}^{H2}\right]
\]

which can be calculated either by SIM or perturbation theory. The first order contribution to this non–additive term

\[
\left(\frac{3}{2} E_{GHL}^{1}\right)_{\text{exch}} = 2\epsilon_{123} - \left[\epsilon_{12}^{1} - \epsilon_{12}^{H2,1}\right] - \left[\epsilon_{23}^{1} - \epsilon_{23}^{H2,1}\right] - \left[\epsilon_{13}^{1} - \epsilon_{13}^{H2,1}\right]
\]

differs from the respective SRS–term Eq. (11) only by overlap integrals that are negligible compared to one.

A comparison of the numerical results of the first order non–additive exchange energy Eq. (11) of SRS theory and the GHL term [Eq. (14)] calculated by SIM using the zeroth order product wave function \( F = 1/\pi^{3/2} \exp(-r_{1A} - r_{2B} - r_{3C}) \) is given in Tables I and II and will be discussed in the next Section.

In summary, the complete three–body exchange effect in \( H_3 \), which consists of the cyclic exchange energy and the effect of the presence of the third atom on the two–body exchange energies, can asymptotically be approximated by the surface integral for the cyclic exchange energy.

VI. RESULTS

In Tables I and II as well as Figures 1 and 2 the numerical results for the first order non–additive exchange energy of SRS theory are compared with three different SIM–terms: (i) the non–additive exchange energy of GHL theory Eq. (13), (ii) the cyclic exchange energy (complete SIM expression Eq. (12) with overlaps), (iii) the surface integral (SI) of the cyclic exchange energy only (without overlaps). All these quantities have been calculated using the zeroth order localized wave function \( F = 1/\pi^{3/2} \exp(-r_{1A} - r_{2B} - r_{3C}) \). Since the exchange energies calculated by SIM cannot be given a definite perturbative order (due to the fact that only part of the complete space is used in the calculation) the quantity (i) is not expected to yield the same numerical results as the first order non–additive exchange energy of SRS theory. But since the same zeroth order product wave function was used to calculate both
terms it is expected that both quantities exhibit a similar overall behavior in the range of parameters studied.

In Table I results for equilateral triangular geometry of the nuclei ranging between \( R = 4 \) and \( R = 10 \) atomic units are listed. Generally, all terms calculated by SIM have smaller absolute values than the first order perturbative ones. At \( R = 4 \) a.u., the absolute value of the complete SIM term Eq. (43) is 27 % below the SRS result Eq. (41), the cyclic exchange energy is 38 % smaller, and only the surface integral of the cyclic exchange energy is 25 % greater in absolute value. At \( R = 10 \) a.u., however, all three quantities calculated by SIM are no longer distinguishable and are only 6 % below the SRS result.

In Table II the results for isosceles triangles with equal sides of length of 6 a.u. and with angles \( \gamma_B \) varying between 30° and 180° are shown. All quantities except for the surface integral without overlaps exhibit a change of sign in the region around 120° and 150°. At 30°, (i) the absolute value of the SIM term Eq. (43) is 31 % smaller than the SRS result, (ii) the cyclic exchange energy is 41 % smaller, and again (iii) the surface integral of the cyclic exchange energy only is 13 % greater in absolute value. At 180° on the other hand, only the value for the surface integral has the wrong sign, while both the other terms have become indistinguishable and are now 35 % greater in absolute value than the SRS term. The differences between the numerical results for the quantities compared in Tables I and II are, as already pointed out, not due to numerical problems but due to the fact that the quantities are different by definition.

From the Tables it appears that for triangular geometries of the nuclei and internuclear distances \( R \geq 4 \) a.u. the first order non–additive exchange energy for the quartet state of \( \text{H}_3 \) can be quite well approximated by the surface integral of the cyclic exchange energy. This was stated in Ref. [14] and has now been explained by the fact that all the SIM approximations (see section V and in Ref. [14]) hold in this region.

In Tables III and IV as well as Figures 1 and 2 higher orders of SRS theory are also taken into account and compared with the complete GHL non–additive exchange energy Eq. (43) in order to show that SIM goes beyond the first order of SRS theory. For equilateral triangular geometries of the nuclei and internuclear distances larger than 6 a.u. the results of GHL theory lie between the first order SRS term and the sum of the first and second order terms, approaching the first order term for increasing distances. At 6 a.u. GHL is very close to the first plus second order of SRS, and even at 4 a.u. GHL is only 17 % below the total sum up to third order of SRS theory.

For isosceles structures of the nuclei with equal internuclear distances of 6 a.u. the advantage of SIM over the first order SRS theory is even more apparent. Starting at 60°, the GHL result is closer to the first plus second order than to the first order SRS term. The change of sign occurs for the first order between 120° and 150° whereas for all other terms already between 90° and 120°. The differences of the GHL to the first plus second order SRS term range from 0.4% at 60° to 33% at 120° and 10% at 180°. At 30° the GHL result is again only 16% smaller than the SRS term with the third order term included.

The advantage of SIM over the perturbative approach is that the surface integral SI is easily calculated numerically, and including the partial overlap terms provides part of the second order SRS contributions.
VII. CONCLUSIONS

This paper demonstrates how the perturbation series consisting of Coulomb, exchange and overlap integrals can be used to express the Coulomb and exchange energies occurring in GHL theory. Combining the perturbation series with the GHL theory yields an energy expression for the quartet spin state equivalent to that of symmetrized Rayleigh–Schrödinger perturbation theory given in [10].

It is possible to evaluate the exchange energies using the surface integral method (SIM). The SIM has the advantage that it derives from a clear physical picture for the exchange process in terms of the electrons continuously trading places. For the cyclic exchange energies this method has already been described in detail in Ref. [14], and for the implicit three–body effect on the two–body exchange energies it will be shown in Ref. [18].

The long range behavior of the three–body terms entering the two–body exchange energies and of the partial overlap integrals — multiplied by two–body exchange energies in the expression for the cyclic exchange energy in Eq. (42) — indicate that for large internuclear separations the surface integral for the cyclic exchange energy is sufficient to describe the non–additive contribution to the exchange part of the quartet spin state. The numerical results in Tables I and II confirm this conclusion.

VIII. ACKNOWLEDGEMENTS

We thank K. T. Tang and J. P. Toennies for helpful discussions. U. K. gratefully acknowledges financial support from the DFG.
REFERENCES

[1] K. T. Tang, J. P. Toennies and C. L. Yiu, Int. Rev. Phys. Chem. 17, 363 (1998).
[2] S. H. Patil and K. T. Tang, Asymptotic Methods in Quantum Mechanics: Applications to Atoms, Molecules and Nuclei (Springer, Berlin, 2000).
[3] U. Kleinekathöfer, K. T. Tang, J. P. Toennies, and C. L. Yiu, J. Chem. Phys. 111, 3377 (1999).
[4] U. Kleinekathöfer, Chem. Phys. Lett 324, 403 (2000).
[5] B. M. Axilrod and E. Teller, J. Chem. Phys. 11, 299 (1943); Y. Muto, Proc. Phys. Soc. Jpn. 17, 629 (1943).
[6] M. J. Elrod and R. J. Saykally, Chem. Rev. 94, 1975 (1994).
[7] W. J. Meath and M. Koulis, J. Mol. Struct. (Theochem.) 226, 1 (1991).
[8] W. J. Meath and R. A. Aziz, Mol. Phys. 52, 225 (1984).
[9] R. Moszynski, P. E. S. Wormer, B. Jeziorski, and A. van der Avoird, J. Chem. Phys. 103, 8058 (1995).
[10] T. Korona, R. Moszynski, and B. Jeziorski, J. Chem. Phys. 105, 8178 (1996).
[11] V. F. Lotrich and K. Szalewicz, J. Chem. Phys. 112, 112 (2000).
[12] R. J. Wheatley, Mol. Phys. 84, 899 (1995).
[13] Z. C. Zhang, A. R. Allnatt, J. D. Talman, and W. J. Meath, Mol. Phys. 81, 1425 (1994).
[14] U. Kleinekathöfer, T. I. Sachse, K. T. Tang, J. P. Toennies, and C. L. Yiu, J. Chem. Phys. 113, 948 (2000).
[15] K. T. Tang, J. P. Toennies, and C. L. Yiu, J. Chem. Phys. 94, 7266 (1991).
[16] K. T. Tang, J. P. Toennies and C. L. Yiu, J. Chem. Phys. 99, 377 (1993).
[17] U. Kleinekathöfer, K. T. Tang, J. P. Toennies, and C. L. Yiu, J. Chem. Phys. 107, 9502 (1997).
[18] T. I. Sachse, K. T. Tang and J. P. Toennies, in preparation.
[19] T. Cwiok, B. Jeziorski, W. Kołos, R. Moszynski, J. Rychlewski und K. Szalewicz, Chem. Phys. Lett. 195, 67 (1992).
[20] J. O. Hirschfelder, Chem. Phys. Lett. 1, 325 (1967).
[21] B. Jeziorski, R. Moszynski, and K. Szalewicz, Chem. Rev. 94, 1887 (1994).
[22] G. Chalasinski, B. Jeziorski, and K. Szalewicz, Int. J. Quantum Chem. 11, 247 (1977).
[23] K. T. Tang, J. P. Toennies, and C. L. Yiu, Chem. Phys. Lett. 162, 170 (1989).
[24] The explicit expressions will be given in a forthcoming paper [18].
TABLES

| $R[^a_0]$ | SRS Eq. (41) | GHL Eq. (43) | $E_{exch}^1[E_h]$ | $2\epsilon_{123}$ (SIM) | $2\ SI$ |
|------------|---------------|---------------|---------------------|----------------------|--------|
| 4          | $-3.83 \cdot 10^{-3}$ | $-2.79 \cdot 10^{-3}$ | $-2.39 \cdot 10^{-3}$ | $-4.21 \cdot 10^{-3}$ |        |
| 5          | $-5.90 \cdot 10^{-5}$ | $-5.19 \cdot 10^{-5}$ | $-5.15 \cdot 10^{-5}$ | $-5.70 \cdot 10^{-5}$ |        |
| 6          | $-5.88 \cdot 10^{-6}$ | $-5.32 \cdot 10^{-6}$ | $-5.31 \cdot 10^{-6}$ | $-5.55 \cdot 10^{-6}$ |        |
| 7          | $-5.33 \cdot 10^{-7}$ | $-4.89 \cdot 10^{-7}$ | $-4.89 \cdot 10^{-7}$ | $-4.98 \cdot 10^{-7}$ |        |
| 8          | $-3.6 \cdot 10^{-9}$ | $-3.4 \cdot 10^{-9}$ | $-3.4 \cdot 10^{-9}$ | $-3.4 \cdot 10^{-9}$ |        |

**TABLE I.** Comparison of the numerical results for the first order non–additive exchange energy of SRS–theory (SRS$_1$ Eq. (41)) with a similar but still different quantity derived from GHL theory Eq. (43), with the cyclic exchange calculated by SIM ($2\epsilon_{123}$ (SIM)) including overlaps, and with the surface integral SI of the cyclic exchange energy without overlaps (2 SI). The nuclei form equilateral triangles with sides of lengths $R$.

| $\gamma_B$ [degrees] | SRS Eq. (41) | GHL Eq. (43) | $E_{exch}^1[E_h]$, $R_{AB} = R_{BC}$ = 6 a.u. | $2\epsilon_{123}$ (SIM) | $2\ SI$ |
|-----------------------|---------------|---------------|-----------------------------------------------|----------------------|--------|
| 30                    | $-3.75 \cdot 10^{-4}$ | $-2.60 \cdot 10^{-4}$ | $-2.23 \cdot 10^{-4}$ | $-4.25 \cdot 10^{-4}$ |        |
| 60                    | $-5.90 \cdot 10^{-5}$ | $-5.19 \cdot 10^{-5}$ | $-5.15 \cdot 10^{-5}$ | $-5.70 \cdot 10^{-5}$ |        |
| 90                    | $-7.40 \cdot 10^{-6}$ | $-6.05 \cdot 10^{-6}$ | $-6.03 \cdot 10^{-6}$ | $-7.95 \cdot 10^{-6}$ |        |
| 120                   | $-3.42 \cdot 10^{-7}$ | $2.61 \cdot 10^{-7}$ | $2.60 \cdot 10^{-7}$ | $-1.62 \cdot 10^{-6}$ |        |
| 150                   | $8.84 \cdot 10^{-7}$ | $1.31 \cdot 10^{-6}$ | $1.30 \cdot 10^{-6}$ | $-5.83 \cdot 10^{-7}$ |        |
| 180                   | $1.10 \cdot 10^{-6}$ | $1.48 \cdot 10^{-6}$ | $1.48 \cdot 10^{-6}$ | $-4.10 \cdot 10^{-7}$ |        |

**TABLE II.** Comparison of the numerical results of SRS–theory with the same quantities as in Table I. The nuclei form isosceles triangles with two sides of lengths $R_{AB} = R_{BC}$ = 6 a.u., $\gamma_B$ is the angle included.

| $R[^a_0]$ | SRS$_1$ Eq. (41) | SRS$_2$ | SRS$_3$ | GHL Eq. (43) |
|------------|-----------------|----------|----------|---------------|
| 4          | $-3.83 \cdot 10^{-3}$ | $-3.60 \cdot 10^{-3}$ | $-3.34 \cdot 10^{-3}$ | $-2.79 \cdot 10^{-3}$ |
| 6          | $-5.90 \cdot 10^{-5}$ | $-5.21 \cdot 10^{-5}$ | $-5.03 \cdot 10^{-5}$ | $-5.19 \cdot 10^{-5}$ |
| 7          | $-5.88 \cdot 10^{-6}$ | $-4.77 \cdot 10^{-6}$ | $-4.62 \cdot 10^{-6}$ | $-5.32 \cdot 10^{-6}$ |
| 8          | $-5.33 \cdot 10^{-7}$ | $-3.71 \cdot 10^{-7}$ | $-3.57 \cdot 10^{-7}$ | $-4.89 \cdot 10^{-7}$ |
| 10         | $-3.6 \cdot 10^{-9}$ | $-0.7 \cdot 10^{-9}$ | $-0.7 \cdot 10^{-9}$ | $-3.4 \cdot 10^{-9}$ |

**TABLE III.** Comparison of the numerical results for the non–additive exchange energy in GHL theory (GHL Eq. (43)) with the first order non–additive exchange energy of SRS–theory (SRS$_1$ Eq. (41)), with the SRS non–additive exchange energy up to second order (SRS$_2$) [10], and with up to third order SRS$_3$ [10]. The nuclei form equilateral triangles with sides of lengths $R$. 

12
| $\gamma_B$ [degrees] | SRS$_1$ Eq. (41) | SRS$_2$ | SRS$_3$ | GHL Eq. (43) |
|----------------------|------------------|---------|---------|--------------|
| 30 | $-3.75 \times 10^{-4}$ | $-3.33 \times 10^{-4}$ | $-3.08 \times 10^{-4}$ | $-2.60 \times 10^{-4}$ |
| 60 | $-5.90 \times 10^{-5}$ | $-5.21 \times 10^{-5}$ | $-5.03 \times 10^{-5}$ | $-5.19 \times 10^{-5}$ |
| 90 | $-7.40 \times 10^{-6}$ | $-5.67 \times 10^{-6}$ | $-4.98 \times 10^{-6}$ | $-6.05 \times 10^{-6}$ |
| 120 | $-3.42 \times 10^{-7}$ | $3.88 \times 10^{-7}$ | $9.02 \times 10^{-7}$ | $2.61 \times 10^{-7}$ |
| 150 | $8.84 \times 10^{-7}$ | $1.43 \times 10^{-6}$ | $1.88 \times 10^{-6}$ | $1.31 \times 10^{-6}$ |
| 180 | $1.10 \times 10^{-6}$ | $1.63 \times 10^{-6}$ | $2.07 \times 10^{-6}$ | $1.48 \times 10^{-6}$ |

**TABLE IV.** Comparison of the numerical results of GHL–theory with the same quantities as in Table III. The nuclei form isosceles triangles with two sides of lengths $R_{AB} = R_{BC} = 6$ a.u., $\gamma_B$ is the angle included.
FIGURES

FIG. 1. Comparison of different orders of the non–additive exchange energy in SRS theory with the GHL result (filled triangles) calculated with SIM from Eq. (43) for equilateral triangles. The first order SRS contribution is denoted by circles, and with all terms up to second order by open triangles. The stars show twice the surface integral of the cyclic exchange energy.
FIG. 2. Comparison of different orders of the non–additive exchange energy in SRS theory with the GHL result (filled triangles) calculated with SIM from Eq. (43) for isosceles triangles with \( R_{AB} = R_{BC} = 6 \) a.u. as a function of the included angle \( \gamma_B \).

The first order SRS contribution is denoted by circles, and with all terms up to second order by open triangles. The stars show twice the surface integral of the cyclic exchange energy only. Note the change in the energy axis from linear to logarithmic scale.