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Generalized Heitler-London theory for H_3: a comparison of the surface integral method with perturbation theory

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Abstract. The generalized Heitler-London (GHL) theory provides a straightforward way to express the potential energy surface of H_3 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 H_3 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.

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1 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 [5,6] 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 [7–9]. In the GHL approach the potentials can be decomposed into Coulomb and exchange *energies*, whereas in symmetry adapted perturbation theory (SAPT) these interactions are expressed in terms of Coulomb and exchange *integrals* in the manner first introduced by Heitler and London. Recently, SAPT was formulated for the interactions of trimers [10] and has been applied to numerical calculations up to third order for the quartet spin state of H_3 [11] and for the helium-trimer [12]. Other three-body calculations for H_3 are based on Heitler-London type calculations [13] and perturbation calculations making use of Unsöld approximations [14]. 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 [15] was calculated using the surface integral method (SIM) which previously has been applied to two atoms [1,2,4,16–18]. In a forthcoming paper [19] 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 [20]. 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 [11]. 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 numerical results reveal that with the zeroth order wave function the surface integral result contains

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parts of the second order SAPT result and is therefore more efficient.

In Sections 2 and 3 the basic ideas of the GHL theory and polarization approximation are described. In Section 4 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 5 reviews the surface integral method (SIM). Thereafter in Section 6 the advantages of SIM over the perturbation approach will be demonstrated by comparing the numerical results of perturbation theory and SIM.

2 Generalized Heitler-London theory for H_3

The application of generalized Heitler-London theory to H_3 was previously discussed in reference [3]. The generalized Heitler-London theory is based on the following equation which has to be solved:

$$\hat{H}F = \sum_g \epsilon_g \hat{T}(g)F. \tag{1}$$

Here F denotes the localized wave function, *i.e.* each electron is associated with only one nucleus such that the wave function is non-symmetrized, $\hat{T}(g)$ designates a permutation operator for the electron coordinates, and ϵ_g stands for the Coulomb ($g = I$) and exchange energies ($g \neq I$). In the next section it will be shown how the function F can be chosen. Applying results from the theory of the symmetric group, correctly symmetrized wave functions can be projected out of the localized wave function and approximations to the eigenenergies of the Hamiltonian in terms of Coulomb and exchange energies are obtained where the quality of the approximation depends on how much the localized wave function chosen differs from an ideal localized one which is a linear combination of exact eigenfunctions (see Ref. [3] for details). The calculation of the Coulomb and exchange energies is the main part of the theory and the details for the H_3-system are explained in this paper.

In terms of Coulomb and exchange energies the two doublet states of H_3 take the form

$$\begin{aligned} {}^{1/2}E_{\mathrm{GHL}} &= \epsilon_I - \epsilon_{123} \\ &\pm \sqrt{\frac{1}{2}\left[(\epsilon_{12}-\epsilon_{23})^2 + (\epsilon_{23}-\epsilon_{13})^2 + (\epsilon_{13}-\epsilon_{12})^2\right]} \end{aligned} \tag{2}$$

and the quartet state

$${}^{3/2}E_{\mathrm{GHL}} = \epsilon_I - \epsilon_{12} - \epsilon_{23} - \epsilon_{13} + 2\epsilon_{123}. \tag{3}$$

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

3 Polarization approximation and generalized Heitler-London (GHL) theory

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

$$\hat{H} = \hat{H}^0 + \hat{V} \tag{4}$$

using

$$\hat{H}^0 = \hat{H}^0_{\mathrm{A}} + \hat{H}^0_{\mathrm{B}} + \hat{H}^0_{\mathrm{C}} \tag{5}$$

$$\hat{V} = \hat{V}_{\mathrm{AB}} + \hat{V}_{\mathrm{BC}} + \hat{V}_{\mathrm{AC}} \tag{6}$$

where $\hat{H}^0_{\mathrm{A}}, \hat{H}^0_{\mathrm{B}}$ and $\hat{H}^0_{\mathrm{C}}$ are the Hamiltonians of three free hydrogen atoms and $\hat{V}_{\mathrm{AB}}, \hat{V}_{\mathrm{BC}}$ and $\hat{V}_{\mathrm{AC}}$ describe the interaction between atoms A and B, B and C, as well as A and C, respectively. The polarization approximation [21] is based on the equation

$$\hat{H}\chi_{\mathrm{p}} = E_{\mathrm{p}}\chi_{\mathrm{p}} \tag{7}$$

where the polarization wave function χ_{p} and the polarization energy E_{p} can be written as perturbation series

$$\chi_{\mathrm{p}} = \sum_n \phi_n, \tag{8}$$

$$E_{\mathrm{p}} = \sum_n \epsilon_n. \tag{9}$$

The zeroth order polarization wave function ϕ_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 χ_{p}, equation (1) together with the Hamiltonian equation (4) can be written as

$$(\hat{H}^0 + \hat{V})|\sum_{n=0}\phi_n\rangle = \sum_g \epsilon_g \hat{T}(g)|\sum_{n=0}\phi_n\rangle. \tag{10}$$

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

$$\begin{aligned} &(\hat{T}(g)\phi_0, (\hat{H}^0 + \hat{V})\sum_{n=0}\phi_n) = \\ &\qquad \sum_{g'} \epsilon_{g'} (\hat{T}(g)\phi_0, \sum_{n=0}\hat{T}(g')\phi_n) \end{aligned} \tag{11}$$

a system of linear equations can be derived for the Coulomb energy ϵ_I as well as for the exchange energies ϵ_g ($g \neq I$) in terms of Coulomb integrals J, exchange integrals K_g, and overlap integrals S_g. The following notation for the overlap, Coulomb and exchange integrals is used:

$$S_g := \sum_{n=0} S_g^n \tag{12}$$

$$J := \sum_{n=0} J^n \tag{13}$$

$$K_g := \sum_{n=0} K_g^n, \tag{14}$$

where

$$\begin{aligned} S_g^n &:= (\hat{T}(g)\phi_0, \phi_n) && (15)\\ J^n &:= (\phi_0, \hat{V}\phi_{n-1}) && (16)\\ J^0 &= E_0 && (17)\\ K_g^n &:= (\phi_0, \hat{V}\hat{T}(g^{-1})\phi_{n-1}). && (18) \end{aligned}$$

The equalities $S_{g^{-1}}^n = S_g^n$ and $K_{g^{-1}}^n = K_g^n$ hold. Using these definitions equation (11) becomes

$$\begin{aligned} E_0 + J &= \epsilon_I + \textstyle\sum_{g' \neq I} \epsilon_{g'} S_{g'^{-1}}: \quad g = I\\ E_0 S_g + K_g &= \epsilon_g + \textstyle\sum_{g' \neq g} \epsilon_{g'} S_{g'^{-1}g}: \quad g \neq I. \end{aligned} \qquad (19)$$

These equations can be solved for the Coulomb and exchange energies ϵ_I and $\epsilon_g, g \neq I$. The results are given in the Appendix. In practice, the perturbation series will only be taken to a finite order M, and the Coulomb and exchange energies are approximated by equations (A.1–A.3) where all overlap, Coulomb and exchange integrals are only calculated up to order M.

To find on the other hand the mth order contribution to the Coulomb and exchange energies one starts from equations (A.1–A.3) as given in the Appendix and proceeds in the following way: the Coulomb and exchange energies are sums over contributions of all orders, *i.e.* $\epsilon_g = \sum_{n=0} \epsilon_g^n$. The first step is to multiply both sides of the results (A.1–A.3) by the denominator N, which is also a sum over terms of all orders. Now both hand sides can be rearranged into groups of terms of the same perturbative order. These groups on both hand sides are then equated, and the group of mth order can be solved for ϵ_g^m.

The convergence properties of the polarization theory have been extensively discussed for the case of two hydrogen atoms [22]. For low orders it was shown that the perturbation series rapidly converges to the Coulomb energy [20,22–24] 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 [10,11]. We want to emphasize that this is not a rigorously proven statement but it is shown below to give quite accurate results. Since here we are only interested in low orders, especially the first, the expected behavior justifies approximating the localized wave function via the polarization approximation for three hydrogen atoms as well.

4 Equivalence of the GHL and SRS theory for quartet H$_3$

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 equation (4) 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 equation (12) of reference [11] this term is given by

$$\begin{aligned} {}^{3/2}E^1_{\mathrm{SRS}} = N_0^{-1}[\langle\psi_0|\hat{V}(1 - \hat{T}(12) - \hat{T}(23)\\ - \hat{T}(13) + \hat{T}(123) + \hat{T}(132))|\psi_0\rangle], \end{aligned} \qquad (20)$$

which can be expressed with equations (15–18) as

$${}^{3/2}E^1_{\mathrm{SRS}} = N_0^{-1}\left[J^1 - K^1_{12} - K^1_{23} - K^1_{13} + K^1_{123} + K^1_{132}\right], \qquad (21)$$

where

$$N_0 = 1 - S^0_{12} - S^0_{23} - S^0_{13} + S^0_{123} + S^0_{132}. \qquad (22)$$

Using equation (19) and the identity $\epsilon_I^0 = E_0$ it is possible to express the first order contributions as

$$\begin{aligned} J^1 = \epsilon^1_I + \epsilon^1_{12}S^0_{12} + \epsilon^1_{23}S^0_{23}\\ + \epsilon^1_{13}S^0_{13} + \epsilon^1_{123}S^0_{123} + \epsilon^1_{132}S^0_{123} \end{aligned} \qquad (23)$$

$$\begin{aligned} K^1_{12} = \epsilon^1_{12} + \epsilon^1_I S^0_{12} + \epsilon^1_{23}S^0_{123}\\ + \epsilon^1_{13}S^0_{123} + \epsilon^1_{123}S^0_{23} + \epsilon^1_{132}S^0_{13} \end{aligned} \qquad (24)$$

$$\begin{aligned} K^1_{23} = \epsilon^1_{23} + \epsilon^1_I S^0_{23} + \epsilon^1_{12}S^0_{123}\\ + \epsilon^1_{13}S^0_{123} + \epsilon^1_{123}S^0_{13} + \epsilon^1_{132}S^0_{12} \end{aligned} \qquad (25)$$

$$\begin{aligned} K^1_{13} = \epsilon^1_{13} + \epsilon^1_I S^0_{13} + \epsilon^1_{12}S^0_{123}\\ + \epsilon^1_{23}S^0_{123} + \epsilon^1_{123}S^0_{12} + \epsilon^1_{132}S^0_{23} \end{aligned} \qquad (26)$$

$$\begin{aligned} K^1_{123} = \epsilon^1_{123} + \epsilon^1_I S^0_{123} + \epsilon^1_{12}S^0_{23}\\ + \epsilon^1_{23}S^0_{13} + \epsilon^1_{13}S^0_{12} + \epsilon^1_{132}S^0_{123} \end{aligned} \qquad (27)$$

$$\begin{aligned} K^1_{132} = \epsilon^1_{132} + \epsilon^1_I S^0_{123} + \epsilon^1_{12}S^0_{13}\\ + \epsilon^1_{23}S^0_{12} + \epsilon^1_{13}S^0_{23} + \epsilon^1_{123}S^0_{123}. \end{aligned} \qquad (28)$$

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

$$\begin{aligned} {}^{3/2}E^1_{\mathrm{SRS}} &= N_0^{-1}\left[J^1 - K^1_{12} - K^1_{23} - K^1_{13} + K^1_{123} + K^1_{132}\right]\\ &= \epsilon^1_I - \epsilon^1_{12} - \epsilon^1_{23} - \epsilon^1_{13} + \epsilon^1_{123} + \epsilon^1_{132} = {}^{3/2}E^1_{\mathrm{GHL}}. \end{aligned} \qquad (29)$$

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 equation (12) of [11] the general nth-order expression for the interaction energy in SRS theory is found to be

$$\begin{aligned}
{}^{3/2}E^n_{\mathrm{SRS}} &= N_0^{-1}\Big[\langle\psi_0|\hat{V}(1-\hat{T}(12)-\hat{T}(23)\\
&\quad -\hat{T}(13)+\hat{T}(123)+\hat{T}(132))|\psi^{(n-1)}_{\mathrm{pol}}\rangle\\
&\quad -\sum_{k=1}^{n-1}{}^{3/2}E^k_{\mathrm{SRS}}\langle\psi_0|(1-\hat{T}(12)-\hat{T}(23)\\
&\quad -\hat{T}(13)+\hat{T}(123)+\hat{T}(132))|\psi^{(n-k)}_{\mathrm{pol}}\rangle\Big]\\
&= N_0^{-1}\,[J^n-K^n_{12}-K^n_{23}-K^n_{13}+K^n_{123}\\
&\quad +K^n_{132}-\sum_{k=1}^{n-1}{}^{3/2}E^k_{\mathrm{SRS}}(-S^{n-k}_{12}\\
&\quad -S^{n-k}_{23}-S^{n-k}_{13}+S^{n-k}_{123}+S^{n-k}_{132})]
\end{aligned}\tag{30}$$

where N_0 is given by equation (22). Thus it is necessary to prove that

$$\begin{aligned}
{}^{3/2}E^n_{\mathrm{GHL}} &= \epsilon^n_I-\epsilon^n_{12}-\epsilon^n_{23}-\epsilon^n_{13}+\epsilon^n_{123}+\epsilon^n_{132} &&(31)\\
&= {}^{3/2}E^n_{\mathrm{SRS}}. &&(32)
\end{aligned}$$

To perform a proof by induction it is necessary to show that also the $(n+1)$th order terms of both theories are equal. To do so, the $(n+1)$th order of GHL theory is expressed in terms of the quantities occurring in SRS theory. This can be achieved by inserting the solutions of the set of linear equations (19) into the complete GHL energy for the H_3-quartet state

$${}^{3/2}E_{\mathrm{GHL}} = \epsilon_I-\epsilon_{12}-\epsilon_{23}-\epsilon_{13}+\epsilon_{123}+\epsilon_{132}\tag{33}$$

and up to Mth order

$$\begin{aligned}
\sum_{n=0}^{M}{}^{3/2}E^n_{\mathrm{GHL}} &= \sum_{n=0}^{M}\Big[\epsilon^n_I-\epsilon^n_{12}-\epsilon^n_{23}-\epsilon^n_{13}+\epsilon^n_{123}+\epsilon^n_{132}\Big]\\
&= E_0+\Big[J-K_{12}-K_{23}-K_{13}+K_{123}+K_{132}\Big]\\
&\quad\times\Big[1-S_{12}-S_{23}-S_{13}+S_{123}+S_{132}\Big]^{-1}
\end{aligned}\tag{34}$$

where J, K_g, and S_g have been defined in equations (12–14). To find the expression for the $(n+1)$th order contribution to the energy of the quartet state, both sides are first multiplied by the denominator

$$\begin{aligned}
&\Big(\sum_{n=0}^{M}{}^{3/2}E^n_{\mathrm{GHL}}\Big)\Big[1-\sum_{n=0}^{M}(S^n_{12}+S^n_{23}+S^n_{13})\\
&\quad+\sum_{n=0}^{M}(S^n_{123}+S^n_{132})\Big] = E_0\Big[1-\sum_{n=0}^{M}(S^n_{12}+S^n_{23}+S^n_{13})\\
&\quad+\sum_{n=0}^{M}(S^n_{123}+S^n_{132})\Big]+\sum_{n=0}^{M}\Big[J^n-K^n_{12}\\
&\quad-K^n_{23}-K^n_{13}+K^n_{123}+K^n_{132}\Big].
\end{aligned}\tag{35}$$

Collecting terms of $(n+1)$th order leads to

$$\begin{aligned}
&{}^{3/2}E^{n+1}_{\mathrm{GHL}}\,(1-S^0_{12}-S^0_{23}-S^0_{13}+S^0_{123}+S^0_{132}) = J^{n+1}\\
&\quad-K^{n+1}_{12}-K^{n+1}_{23}-K^{n+1}_{13}+K^{n+1}_{123}+K^{n+1}_{132}\\
&\quad+E_0(-S^{n+1}_{12}-S^{n+1}_{23}-S^{n+1}_{13}+S^{n+1}_{123}+S^{n+1}_{132})\\
&\quad-\sum_{k=0}^{n}{}^{3/2}E^k_{\mathrm{GHL}}(-S^{n+1-k}_{12}-S^{n+1-k}_{23}\\
&\quad-S^{n+1-k}_{13}+S^{n+1-k}_{123}+S^{n+1-k}_{132})
\end{aligned}\tag{36}$$

with the result that

$$\begin{aligned}
{}^{3/2}E^{n+1}_{\mathrm{GHL}} &= N_0\Big[J^{n+1}-K^{n+1}_{12}-K^{n+1}_{23}\\
&\quad-K^{n+1}_{13}+K^{n+1}_{123}+K^{n+1}_{132}\\
&\quad-\sum_{k=1}^{n}{}^{3/2}E^k_{\mathrm{GHL}}(-S^{n+1-k}_{12}-S^{n+1-k}_{23}\\
&\quad-S^{n+1-k}_{13}+S^{n+1-k}_{123}+S^{n+1-k}_{132})\Big].
\end{aligned}\tag{37}$$

Using the claim of the proof, which stated that for all orders up to the nth the GHL term is equal to the SRS-term, ${}^{3/2}E^k_{\mathrm{GHL}}$ in the last line can be replaced by ${}^{3/2}E^k_{\mathrm{SRS}}$ for all orders $k=1,...,n$. Thus equation (37) can be transformed into

$$\begin{aligned}
{}^{3/2}E^{n+1}_{\mathrm{GHL}} &= N_0\Big[J^{n+1}-K^{n+1}_{12}\\
&\quad-K^{n+1}_{23}-K^{n+1}_{13}+K^{n+1}_{123}+K^{n+1}_{132}\\
&\quad-\sum_{k=1}^{n}{}^{3/2}E^k_{\mathrm{SRS}}(-S^{n+1-k}_{12}-S^{n+1-k}_{23}\\
&\quad-S^{n+1-k}_{13}+S^{n+1-k}_{123}+S^{n+1-k}_{132})\Big] &&(38)\\
&= {}^{3/2}E^{n+1}_{\mathrm{SRS}} &&(39)
\end{aligned}$$

and the equality also holds for the $(n+1)$th 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 reference [11], 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 equations (23) and

(55) of reference [10] is given by

$$\begin{aligned}E^1_{\rm exch}(3,3) &= \langle\psi_0|\hat V_{\rm AB}\Big(\hat T(23)+\hat T(13)+\hat T(123)\\&\quad+\hat T(132)-S^0_{23}-S^0_{13}-S^0_{123}-S^0_{132}\Big)|\psi_0\rangle\\&\quad+\langle\psi_0|\hat V_{\rm BC}\Big(\hat T(12)+\hat T(13)+\hat T(123)+\hat T(132)\\&\quad-S^0_{12}-S^0_{13}-S^0_{123}-S^0_{132}\Big)|\psi_0\rangle\\&\quad+\langle\psi_0|\hat V_{\rm AC}\Big(\hat T(12)+\hat T(23)+\hat T(123)+\hat T(132)\\&\quad-S^0_{12}-S^0_{23}-S^0_{123}-S^0_{132}\Big)|\psi_0\rangle. \qquad (40)\end{aligned}$$

This can be expressed in terms of exchange energies as

$$\begin{aligned}E^1_{\rm exch}(3,3) &= 2\epsilon^1_{123}(1-S^0_{123})\\&\quad-\Big[\epsilon^1_{12}(1+S^0_{12})-\epsilon^{H_2,1}_{12}(1+S^0_{12})\Big]\\&\quad-\Big[\epsilon^1_{23}(1+S^0_{23})-\epsilon^{H_2,1}_{23}(1+S^0_{23})\Big]\\&\quad-\Big[\epsilon^1_{13}(1+S^0_{13})-\epsilon^{H_2,1}_{13}(1+S^0_{13})\Big]. \qquad (41)\end{aligned}$$

The same result can also be obtained by subtracting the pure two-body contributions from equation (29).

5 Surface integral method (SIM) for the calculation of exchange energies

As shown in reference [15] 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 ϵ_{g_0} associated with the arbitrary group element $g_0 \neq I$ is given accordingly by

$$\begin{aligned}\varepsilon_{g_0} &= \left[\int_V {\rm d}v\Big[F^2-(\hat T(g_0)F)^2\Big]\right]^{-1}\\&\quad\times\left[\frac{1}{2}\int_\Sigma\Big\{F\boldsymbol\nabla^{(9)}\Big[\hat T(g_0)F\Big]-\Big[\hat T(g_0)F\Big]\boldsymbol\nabla^{(9)}F\Big\}\cdot{\rm d}\boldsymbol s\right.\\&\quad\left.-\sum_{g\neq I,g_0}\varepsilon_g\int_V{\rm d}v\Big[F(\hat T(g_0g)F)-(\hat T(g_0)F)(\hat T(g)F)\Big]\right]. \qquad (42)\end{aligned}$$

Here V denotes a 9-dimensional partial volume which is not equal to the full space and Σ denotes its 8-dimensional surface. $\boldsymbol\nabla^{(9)}$ is an abbreviated symbol for the gradient operators which appear in the kinetic energy operators of the three electrons $\boldsymbol\nabla^{(9)}=(\boldsymbol\nabla_1,\boldsymbol\nabla_2,\boldsymbol\nabla_3)$. As explained in reference [15] the partial volume V can be chosen such that the wave function F is localized inside.

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 reference [15] 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 equation (42) go to zero with at least a factor of ${\rm e}^{-R}$ faster than the surface integral itself. R denotes the smallest internuclear distance for the respective nuclear geometry. This holds for all exchange energies. In a forthcoming paper [19] it will be shown how to find the implicit three-body effect from the complete surface integral expression equation (42) for the two-body exchange energies. For product wave functions as used here the pure two-body part is given by the second line of equation (42), *i.e.* surface integral (SI) over denominator. The implicit three-body effect is contained in the third line of equation (42), *i.e.* the products of partial overlap integrals with exchange energies. Following the same scheme used in the Appendix of reference [15], these terms can be shown to asymptotically go to zero as ${\rm e}^{-5R}$ which is faster by a factor of ${\rm e}^{-3R}$ 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 equation (3)

$$\begin{aligned}({}^{3/2}E_{\rm GHL})_{\rm exch} &= 2\epsilon_{123}-\Big[\epsilon_{12}-\epsilon^{H_2}_{12}\Big]\\&\quad-\Big[\epsilon_{23}-\epsilon^{H_2}_{23}\Big]-\Big[\epsilon_{13}-\epsilon^{H_2}_{13}\Big] \qquad (43)\end{aligned}$$

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

$$\begin{aligned}({}^{3/2}E^1_{\rm GHL})_{\rm exch} &= 2\epsilon^1_{123}-\Big[\epsilon^1_{12}-\epsilon^{H_2,1}_{12}\Big]\\&\quad-\Big[\epsilon^1_{23}-\epsilon^{H_2,1}_{23}\Big]-\Big[\epsilon^1_{13}-\epsilon^{H_2,1}_{13}\Big] \qquad (44)\end{aligned}$$

differs from the respective SRS-term equation (40) only by overlap integrals that are negligible compared to one for the nuclear geometries used here.

A comparison of the numerical results of the first order non-additive exchange energy equation (40) of SRS theory and the GHL term (Eq. (44)) calculated by SIM using the zeroth order product wave function $F=\pi^{-3/2}\exp(-r_{1\rm A}-r_{2\rm B}-r_{3\rm C})$ is presented and 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.

Table 1. Comparison of the numerical results for the non-additive exchange energy in GHL theory (GHL, Eq. (43)) and twice the surface integral without overlaps with the first order non-additive exchange energy of SRS-theory (SRS_1, Eq. (40)), with the SRS non-additive exchange energy up to second order (SRS_2) [11] , and with up to third order SRS_3 [11]. The nuclei form equilateral triangles with sides of lengths R.

	$E_{\mathrm{exch}}[E_h]$				
$R[a_0]$	SRS_1 Eq. (40)	SRS_2	SRS_3	GHL Eq. (43)	2 × SIM without overlaps
4	-3.83×10^{-3}	-3.60×10^{-3}	-3.34×10^{-3}	-2.79×10^{-3}	-4.21×10^{-3}
6	-5.90×10^{-5}	-5.21×10^{-5}	-5.03×10^{-5}	-5.19×10^{-5}	-5.70×10^{-5}
7	-5.88×10^{-6}	-4.77×10^{-6}	-4.62×10^{-6}	-5.32×10^{-6}	-5.88×10^{-6}
8	-5.33×10^{-7}	-3.71×10^{-7}	-3.57×10^{-7}	-4.89×10^{-7}	-5.33×10^{-7}
10	-3.6×10^{-9}	-0.7×10^{-9}	-0.7×10^{-9}	-3.4×10^{-9}	-3.4×10^{-9}

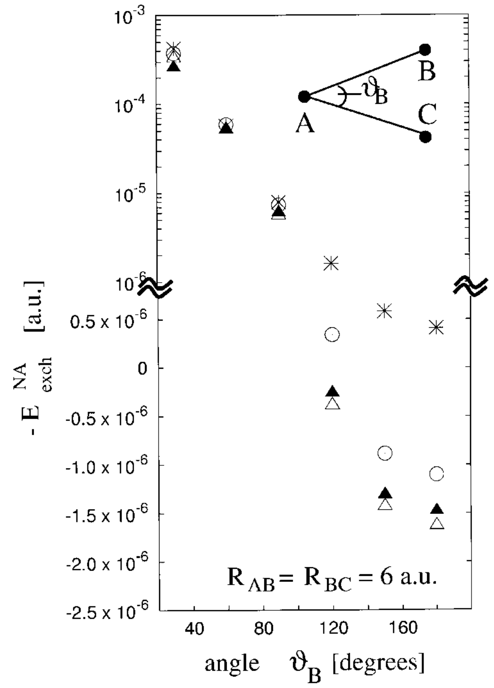

Fig. 1. Comparison of different orders of the non-additive exchange energy in SRS theory with the GHL result (filled triangles) calculated with SIM from equation (43) for isoceles triangles with $R_{\mathrm{AB}} = R_{\mathrm{BC}} = 6$ a.u. as a function of the included angle γ_{B}. The first order SRS contribution is denoted by circles, and the sum of the first and second order terms by open triangles. The stars show twice the surface integral of the cyclic exchange energy without overlaps. Note the change in the energy axis from linear to logarithmic scale.

6 Results

In Figure 1 and Table 1 the numerical results for the first orders of the non-additive exchange energy of SRS theory are compared with two different SIM-terms: (i) the non-additive exchange energy of GHL theory equation (43), and (ii) the surface integral (SI) of the cyclic exchange energy only (without overlaps). The GHL quantities and the first order SRS term have been calculated using the same zeroth order localized wave function $F = \pi^{-3/2} \exp(-r_{1\mathrm{A}} - r_{2\mathrm{B}} - r_{3\mathrm{C}})$. 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 quantities (i) and (ii) are 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 all three terms it is expected that the quantities exhibit a similar overall behavior in the range of parameters studied. This is similar to the difference between the first-order exchange integral in H_2 and the exchange energy calculated with the zeroth-order localized wave function which was discussed previously (see Ref. [17]). In H_2, the first-order exchange integral is known to behave unphysically for large separations whereas the exchange energy is very close to what is believed to be the exact result [25,26] although both terms are calculated using the same zeroth-order wave function.

In Table 1 results for equilateral triangular geometry of the nuclei ranging between $R = 4$ and $R = 10$ atomic units are shown. 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 equation (43) is 27% below the SRS result equation (40), and the surface integral of the cyclic exchange energy without overlaps is 25% greater in absolute value. At $R = 10$ a.u., however, both quantities calculated by SIM are no longer distinguishable and are only 6% below the SRS result.

In Figure 1 the results for isoceles triangles with equal sides of length of 6 a.u. and with angles γ_{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 equation (43) is 31% smaller than the SRS result, and (ii) the surface integral of the cyclic exchange energy without overlaps is 13% greater in absolute value. At 180° on the other hand, only the value for the surface integral without overlaps has the wrong sign, while the complete GHL term has changed sign and is now 35% larger in absolute value than the SRS term. The differences between the numerical results for the quantities compared in this figure are, as already pointed out, not due to numerical problems but due to the fact that the quantities are different by definition.

From these results 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 H_3 can be quite well approximated by the surface integral of the cyclic exchange energy without overlap. This was stated in reference [15] and has now been explained by the fact that all the SIM approximations (see Sect. 5 and Ref. [15]) hold in this region.

In Figure 1 and Table 1 higher orders of SRS theory are also taken into account and compared with the complete GHL non-additive exchange energy equation (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 isoceles 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 (see Fig. 1). 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°.

The differences between the two approaches, perturbation theory and surface integral method, to calculate the non-additive exchange energy using the same zero-order wave functions are similar to what was found previously for the exchange in H_2. In H_2, the surface integral result was nearly indistinguishable from the exact result by Kolos and Wolniewicz [17,25,26] whereas the perturbative result employing the same wave function exhibited an unphysical behavior. For the non-additive exchange in H_3, no exact result is known, but the surface integral result with the zero-order wave function seems to include contributions of higher than first order. It should be pointed out that in the surface integral approach the only approximation made is the choice of the wave function. Having chosen a wave function, the surface integral expression used for the calculations here is without further approximation directly derived from the generalized Heitler-London equation (1). 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.

7 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 [11].

It is possible to evaluate the exchange energies using the surface integral method (SIM). 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 reference [15], and for the implicit three-body effect on the two-body exchange energies it will be shown in reference [19].

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 equation (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 Figure 1 and Table 1 confirm this conclusion.

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Appendix: Perturbation series for the Coulomb and exchange energies

The solution of the system of six linear equations (19) is given by

$$\begin{aligned}\epsilon_I = E_0 + \Big\{ & J\frac{1}{3}[2gu + ab - cd + 2S_{123}(ab - cd - gu)] \\ & - \sum_{i<j} K_{ij}[S_{ij}gu - \frac{1}{6}(g-u)(ab - cd - gu)] \\ & + 2K_{123}\frac{1}{3}[S_{123}(2(ab-cd) + gu) \\ & + ab - cd - gu]\Big\}/N \end{aligned} \tag{A.1}$$

$$\begin{aligned}\epsilon_{ij} = \Big\{ & K_{ij}\frac{1}{3}[2gu + ab - cd + 2S_{123}(ab - cd - gu)] \\ & + J[S_{ij}gu - \frac{1}{6}(g-u)(ab - cd - gu)] \\ & + (K_{ik} + K_{jk})\frac{1}{3}[S_{123}(2(ab-cd) + gu) \\ & + ab - cd - gu]K_{123}[(S_{ik} + S_{jk})gu \\ & + \frac{1}{3}(g-u)(ab - cd - gu)]\Big\}/N \end{aligned} \tag{A.2}$$

$$\begin{aligned}\epsilon_{ijk} = \Big\{ & K_{ijk}\frac{1}{3}[2gu + ab - cd + 2S_{123}(ab - cd - gu)] \\ & - \sum_{i<j} K_{ij}[S_{(ikj)(ij)}gu + \frac{1}{6}(g-u)(ab - cd - gu)] \\ & + (J + K_{ijk})\frac{1}{3}[S_{123}(2(ab-cd) + gu) \\ & + ab - cd - gu]\Big\}/N \end{aligned} \tag{A.3}$$

where

$$\begin{aligned} N &= gu(ab-cd)\\ g &= \sum_{g\in S_3} D^{\mathrm{A}}(g)S_g, \quad u = \sum_{g\in S_3} D^{\mathrm{B}}(g)S_g,\\ a &= \sum_{g\in S_3} D^{\mathrm{E}}_{11}(g)S_g, \quad b = \sum_{g\in S_3} D^{\mathrm{E}}_{22}(g)S_g,\\ c &= \sum_{g\in S_3} D^{\mathrm{E}}_{12}(g)S_g, \quad d = \sum_{g\in S_3} D^{\mathrm{E}}_{21}(g)S_g, \end{aligned} \tag{A.4}$$

and where A is the totally symmetric irreducible representation of S_3, B, the totally antisymmetric and E, the two-dimensional irreducible representation of S_3 (see [3]).

Note that this solution is general in terms of the choice of the zeroth order Hamiltonian. For example, one could choose $\hat{H}^0$ to be the Hamiltonian of an H_2-molecule formed by A and B and a free hydrogen atom C, *i.e.* $\hat{H}^0 = \hat{H}^0_{\mathrm{A}} + \hat{H}^0_{\mathrm{B}} + \hat{V}_{\mathrm{AB}} + \hat{H}^0_{\mathrm{C}}$.

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