What is the exchange-repulsion energy? Insight by partitioning into physically meaningful contributions

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Exchange repulsion, the dominant repulsive contribution to intermolecular interaction energies, is caused by the Pauli principle, which enforces that electrons with the same spin must not be located at the same place. Starting from the Heitler-London expression of the exchange-repulsion energy, E_{xr}, we investigate how it can be partitioned into physically relevant and comprehensible contributions. We demonstrate that a division of E_{xr} into a positive kinetic and a negative potential part is possible. However, these contributions correlate only poorly with the actual exchange-repulsion energy. A meaningful partitioning of E_{xr} is derived, where the kinetic energy contribution belongs to a term that vanishes for exact Hartree-Fock wave functions. The remaining pure potential energy terms are distinguished into an exchange integral contribution, E_{xi}, as well as contributions to the repulsion-energy with two, three and four orbital indices (E_{xr2}, E_{xr3}, and E_{xr4}). Qualitative explanations of these terms and their physical origin are proposed. The forms, relationships and absolute sizes of the four parts of E_{xr} suggest an intuitive partitioning of the exchange-repulsion energy into orbital-pair contributions. Insight into the analytic form and quantitative size of the contributions to E_{xr} is provided by considering the $^3\Sigma_u^+$ $(1\sigma_g 1\sigma_u)$ state of the H_2 molecule, the water dimer, as well as an argon atom interacting with Cl_2 and N_2. It is demonstrated that E_{xr} is best described as being due to the potential energy and that its leading contribution, E_{xr2}, provides an intuitive qualitative and quantitative approach towards the exchange-repulsion energy.

I. INTRODUCTION

The interaction energy, E_{int}, of neutral atoms and/or molecules is generally dominated by electrostatic interactions, E_{el}, London dispersion, E_{dsp}, and a repulsive contribution which is designated as (Pitzer) strain, steric hindrance, overlap repulsion, kinetic repulsion, Pauli repulsion, exchange or exchange-repulsion energy, E_{xr}.[1–5] Additionally, induction (polarization), charge-transfer, hyperconjugation and covalent contributions to the interaction energy are frequently considered.[6–11] As the dominant repulsive interaction, exchange-repulsion provides generally a large positive contribution to the interaction energy. At the minimum structures of molecular dimers, E_{xr} is generally larger than the (absolute) interaction energy, E_{int}.[5,12] In any case the exchange-repulsion energy is a crucial contribution to E_{int} as it determines the space that is required by atoms or molecules in condensed matter. E_{xr} essentially depends on the overlap of the orbitals of the interacting systems and decays exponentially with their distance. In force fields it is commonly approximated by atom centered potentials as proposed by e.g. Lennard-Jones[13–15] or Born and Mayer.[16,17] Even though significant effort has been spent to improve this description (see e.g.[18–20]), such force fields often have problems in correctly predicting molecular crystal and aggregate structures.[21–25] Recent investigations concluded that features in the exchange-repulsion energy that can not be represented by atom centered potentials may be the reason for this failure.[26–34]

While molecular interaction energy, E_{int}, is a physically well-defined property, the above-mentioned energy contributions can only be obtained by an energy decomposition analysis (EDA) which requires an ad hoc definition of energy contributions. A multitude of EDA methods have been published,[11,35–41] but only some of them provide comparable, reliable, physically meaningful, and chemically plausible contributions to the interaction energy of atoms and molecules.[29,42–45] Among these approaches, Symmetry-Adapted Perturbation Theory (SAPT) stands out as a theoretically well-defined method that can be applied at different levels of approximation. It has been shown that SAPT provides physically reasonable results that are in good agreement with the more elaborate EDA variants.[29,43–45] Several empirical and approximate expressions of the exchange-repulsion energy have been proposed (see Ref. 46 for an overview).

Despite the enormous importance of the exchange-repulsion energy for the appearance of matter, our understanding of its origin is surprisingly limited. There is not even agreement in the literature on how the latter results from the underlying electronic structure. Using the Hellmann-Feynman[47,48] theorem, Salem[49] concluded that exchange repulsion is mainly due to potential energy terms. He argued that the Pauli principle enforces a reduction of the electron probability density in regions where electrons from two approaching systems appear simultaneously, which leads to reduced electron-nuclear attraction. In contrast, Baerends[2] showed that antisymmetrization of the orbitals of two approaching systems goes along with an increase of the expectation

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value of the kinetic energy. Other authors supported this point of view by coining the name 'kinetic energy pressure'.[50–52] Szalewicz and Jeziorski[5] argued that the exchange-repulsion energy is due to a tunneling effect and that it can be motivated by additional nodes in the wave functions. As nodes are accompanied by larger curvatures of the wave functions, this suggests that the exchange-repulsion energy is associated with an increase of the kinetic energy. However, in the SAPT approach, which is reviewed in the work of Szalewicz and Jeziorski,[5] the exchange(-repulsion) energy is expressed exclusively by matrix elements of potential energy operators,[53,54] which was already proposed as early as 1936 in the seminal work of Landshoff on the cohesive energy of NaCl.[55]

Thus, we end up in two mutually exclusive statements that the exchange-repulsion energy is either due to kinetic energy terms or free from kinetic energy and thus caused by the potential energy. One may think that this contradiction can be resolved by the virial theorem,[56] which links kinetic and potential contributions to the total energy for stationary structures and indeed applies to the interaction energy.[57] However, the virial theorem is obviously not valid for energy contributions to E_{int} as the electrostatic or the exchange-repulsion energy. The question why the exchange-repulsion energy can be represented either with or without kinetic energy contributions has been explained by making use of stationary conditions of the interacting systems[53,57,58] (see also below). We summarize that the exchange repulsion energy is an important but elusive quantum mechanical quantity that is not amenable to a simple interpretation. Furthermore, there is no reliable, physically motivated, and pictorial explanation for this quantity which makes it possible to derive efficient approximations and comprehensible constituents to E_{xr}. This is what we shall try to develop in the following.

For that purpose, we consider the representation of the exchange-repulsion energy by SAPT and the related Heitler-London approach[59] for closed-shell atoms or molecules. The latter has been worked out in the context of intermolecular interactions by Hayes and Stone,[60,61] Tang and Toennies,[62,63] and by others.[64,65] We show that an accurate approximation of the exchange-repulsion energy of two closed-shell systems can be obtained from a few matrix elements of the occupied orbitals of the interacting systems. This allows to separate E_{xr} in a few contributions and provides insight into the physical origin of this interaction. We also formulate the analogous theory for the exchange-repulsion energy of two hydrogen atoms in the open-shell $^3\Sigma_u^+$ $(1\sigma_g 1\sigma_u)$ state. Here the wave functions of the separated systems and their energy expectation values are directly accessible, allowing to analyze numerical and analytic properties of the exchange-repulsion energy. We demonstrate that this allows to interpret contributions to the exchange-repulsion energy and to estimate their relative size. Similar investigations are also presented for several aggregates of closed-shell systems. These results provide an interpretative basis for explaining the physical origin of the repulsive intermolecular forces.

Following this drain of thoughts, this article is organized as follows: In Sec. II, various representations of the exchange-repulsion energy between two closed-shell molecules are presented and the separation of the terms into contributions is discussed. On that basis, we propose in Sec. III an analogous partitioning for the exchange-repulsion energy of the open-shell triplet hydrogen system. Analytical and numerical results of the latter are discussed to aid the interpretation of the contributions, which is provided in Sec. IV. The implementation for closed-shell systems is described in Sec. V and results for the energy contributions to E_{xr} for several water dimer structures as well as for the interaction of an argon atom with either a nitrogen or a chlorine molecule are given in Sec. VI. Finally, Sec. VII concludes and provides an assessment of the information gained on the exchange-repulsion energy.

II. THE EXCHANGE-REPULSION ENERGY FOR CLOSED SHELL SYSTEMS

Hayes and Stone[60,61] derived analytical expressions for the energy contributions of two interacting subsystems (atoms, molecules, or ions) A and B. In the following, we make use of these expressions and assume that the wave functions of these individual systems are represented by closed shell Slater determinants with Hartree-Fock orbitals. The occupied orbitals of system A and B are orthonormal and may be chosen to be eigenfunctions of the respective Fock operator. However, we shall only make use of this if explicitly stated. Orbitals of system A are generally non-orthogonal to the orbitals on B. The energy expectation value of a Slater determinant consisting of these orbitals is given by[60,61]

$$E_{\text{tot}} = \sum_{ij} 2(i|\hat{T} + \hat{V}_A + \hat{V}_B|j) S^{-1}_{ji} + \sum_{ijkl} [2(ij|kl) - (il|jk)] S^{-1}_{ij} S^{-1}_{kl} + V_{AA} + V_{AB} + V_{BB}, \tag{1}$$

where $\hat{V}_A$ $(\hat{V}_B)$ is the electron nuclear attraction operator comprising all nuclei at molecule A (B), $\hat{T}$ is the kinetic energy operator, $(ij|kl)$ a two electron integral in charge density (Mulliken) notation $(ij|kl) =$

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$\iint \psi_i^*(\vec{r}_1)\psi_j(\vec{r}_1)\frac{1}{r_{12}}\psi_k^*(\vec{r}_2)\psi_l(\vec{r}_2)\,\mathrm{d}\vec{r}_1\,\mathrm{d}\vec{r}_2$ where the indices i, j, k, and l run over all occupied spatial orbitals of the dimer system. V_{XY} represents the nuclear repulsion energy of all nuclei in the subsystems X and Y. Note, that the matrix elements of the inverse overlap matrix S_{ij}^{-1} are required to evaluate this energy expectation value, where the overlap matrix is $S_{ij} = (i|j)$.

$$E_{\mathrm{xr}} = E_{\mathrm{tot}} - E_A - E_B - E_{\mathrm{el}}. \tag{2}$$

Here

$$E_A = \sum_a 2(a|\hat{V}_A + \hat{T}|a) + \sum_{a,a'}[2(aa|a'a') - (aa'|a'a)] + V_{AA}, \tag{3}$$

is the Hartree-Fock energy of monomer A and an analogous formula applies to B. We have deliberately chosen to designate the occupied orbitals on the system A with the indices a and a' and those on B with b and b', as this makes it much easier to associate orbitals with their systems. Note, that a or b stand for occupied (rather than virtual) orbitals and that an index a in a sum is meant to run over all occupied orbitals of system A. With the electrostatic interaction energy

$$E_{\mathrm{el}} = \sum_a 2(a|\hat{V}_B|a) + \sum_b 2(b|\hat{V}_A|b) + \sum_{a,b} 4(aa|bb) + V_{AB}, \tag{4}$$

we obtain the exchange-repulsion energy as[60,61]

$$\begin{aligned} E_{\mathrm{xr}} =& \sum_{ij} 2(i|\hat{T} + \hat{V}_A + \hat{V}_B|j)(S_{ji}^{-1} - \delta_{ji}) + \\ & \sum_{ijkl}[2(ij|kl) - (il|jk)](S_{ij}^{-1}S_{kl}^{-1} - \delta_{ji}\delta_{kl}) \\ & - \sum_{ab} 2(ab|ba), \end{aligned} \tag{5}$$

which is frequently designated as Heitler-London theory.[59,62,63,65] Its kinetic energy contribution can be defined as

$$T_{\mathrm{xr}} = 2\sum_{ij} T_{ij}(S_{ji}^{-1} - \delta_{ji}). \tag{6}$$

The exchange-repulsion energy includes the strictly negative exchange-integral contribution

$$E_{\mathrm{xi}} = \sum_{ab} -2(ab|ba) \tag{7}$$

and the repulsion energy

$$E_{\mathrm{rep}} = E_{\mathrm{xr}} - E_{\mathrm{xi}}. \tag{8}$$

Su and Li[38] designate the result of Eq. (8) as repulsion energy as in the present work, while they refer to the sum over the exchange integrals in Eq. (7) as "exchange energy." However, the very same name is used in SAPT theory to designate an energy contribution corresponding essentially to E_{xr}.[53,54,58,66] Thus, the name "exchange energy" is used for related but very different properties which have even opposite signs. In order to avoid ambiguities, we avoid the term "exchange energy" in the present work and denote E_{xr}, E_{rep}, and E_{xi} in Eqs. (5), (8), and (7) as exchange-repulsion energy, repulsion energy, and exchange-integral contribution, respectively. Our definition of E_{xr} provides essentially the same results as the simplest variant of the repulsive energy from symmetry adapted perturbation theory, SAPT0, which is generally designated as $E_{\mathrm{exch}}^{(1,0)}$.[53,66–69]

The inverse overlap matrix elements in Eq. (5) can be simplified by recognizing that the diagonal elements of the overlap matrix (S_{ii}) are equal to one and that only the non-diagonal matrix elements corresponding to orbitals on the different systems (S_{ab} and S_{ba}) are non-zero. We found that the absolute size of these matrix elements does generally not exceed a value of 0.08 for thermodynamically accessible structures. If we define $\mathbf{P}$ as a matrix containing the non-diagonal matrix elements of $\mathbf{S}$ which means $\mathbf{S} = \mathbf{1} + \mathbf{P}$, the inverse overlap matrix can be expanded in a Taylor series as

$$\mathbf{S}^{-1} = (\mathbf{1} + \mathbf{P})^{-1} = \mathbf{1} - \mathbf{P} + \mathbf{P}^2 \ldots \tag{9}$$

A reasonable expression for the exchange-repulsion energy is obtained by truncating this expansion after the quadratic term which shall be named $E_{\mathrm{xr}}^{P^2}$ in the following. Using the Fock operator of the total system $\hat{F} = \hat{F}_A + \hat{F}_B - \hat{T}$,[70] this approximation to the exchange-repulsion energy can be written as

$$\begin{aligned} E_{\mathrm{xr}}^{P^2} =& E_{\mathrm{xi}} - 2\sum_{ab} 2(a|\hat{F}|b)S_{ba} \\ & + 2\sum_{aa'}(a|\hat{F}|a')\sum_b S_{ab}S_{ba'} + 2\sum_{bb'}(b|\hat{F}|b')\sum_a S_{ba}S_{ab'} \\ & + 2\sum_{aba'b'}\Big[4(ab|a'b') - (ab'|a'b) - (aa'|b'b)\Big]S_{ba}S_{b'a'}. \end{aligned} \tag{10}$$

While Eq. (10) is typically a good approximation for the exchange-repulsion energy in Eq. (5), it is more common

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to neglect all terms which are higher than second order in the differential overlap of the orbitals. This is generally designated as S^2 approximation[53,66,69,71–76] and leads to the exchange-repulsion energy[77]

$$\begin{aligned}
E_{\mathrm{xr}}^{S^2} =& E_{\mathrm{xi}} - 2\sum_{ab} 2(a|\hat{F}|b)S_{ba} \\
&+ 2\sum_{aa'}(a|\hat{F}+\hat{K}_B|a')\sum_{b} S_{ab}S_{ba'} + 2\sum_{bb'}(b|\hat{F}+\hat{K}_A|b')\sum_{a} S_{ba}S_{ab'} \\
&- 2\sum_{aba'b'}(aa'|b'b)S_{ba}S_{b'a'}.
\end{aligned} \tag{11}$$

Here, terms higher than second order in differential overlap such as $(b|\hat{K}_A|b')S_{ab}S_{ba'}$ or $(ab|a'b')S_{ab}S_{a'b'}$ are neglected. In the following we consider $E_{\mathrm{xr}}^{P^2}$ as we shall show that it is more accurate and computationally easier to evaluate. However, we shall also show that the difference between $E_{\mathrm{xr}}^{S^2}$ and $E_{\mathrm{xr}}^{P^2}$ is generally very small, so both are equally appropriate for the accuracy achievable at this level of theory.

The expression for the exchange-repulsion energy in Eq. (10) can be simplified by substituting the total Fock operator by the corresponding monomer operators, $\hat{F}_A$ and $\hat{F}_B$, of the individual systems

$$\begin{aligned}
E_{\mathrm{xr}}^{P^2} = E_{\mathrm{xi}} &+ 2\sum_{ab} S_{ba}\left[-2(a|\hat{F}_A+\hat{F}_B-\hat{T}|b) + \sum_{a'}(a|\hat{F}_A|a')S_{a'b} + \sum_{b'} S_{ab'}(b'|\hat{F}_B|b)\right] \\
&+ 2\sum_{aa'}(a|\hat{F}_B-\hat{T}|a')\sum_{b} S_{ab}S_{ba'} + 2\sum_{bb'}(b|\hat{F}_A-\hat{T}|b')\sum_{a} S_{ba}S_{ab'} \\
&+ 2\sum_{aba'b'}\left[4(ab|a'b') - (ab'|a'b) - (aa'|b'b)\right]S_{ba}S_{b'a'}.
\end{aligned} \tag{12}$$

The kinetic energy contribution to the exchange-repulsion energy defined in Eqs. (10) and (12) is

$$T_{\mathrm{xr}}^{P^2} = 2\sum_{ab} S_{ab}\left[-2T_{ab} + \sum_{a'} T_{aa'}S_{a'b} + \sum_{b'} S_{ab'}T_{b'b}\right]. \tag{13}$$

The latter was discussed by Baerends[2] who neglected the generally minor term $-2T_{ab}S_{ab}$ as the remainder of this expression is typically a much larger and positive contribution. Baerends concluded that the kinetic energy contribution can be considered to be decisive for the repulsive character of the exchange-repulsion energy, which motivates its designation as kinetic repulsion.[2]

However, we shall show below that the kinetic energy contribution generally behaves rather differently than the exchange-repulsion energy. Furthermore, it can be cast into a contribution to the exchange-repulsion energy that vanishes in the limit of a complete basis set[53,57] or if the same basis is used for both systems in the sense of a Boys-Bernardi[78] counterpoise correction.[58] In these cases, the orbitals of the subsystems fulfill the stationary condition of the respective Hartree-Fock equations. Then for canonical orbitals $\hat{F}_A\psi_a = \epsilon_a\psi_a$, where ϵ_a is the orbital energy of the orbital a. Thus, $(b|\hat{F}_A|a) = \epsilon_a\,(b|a)$ and since $\hat{F}_A$ is hermitian, $(a|\hat{F}_A|b) = \epsilon_a\,S_{ab}$ and the orthonormality of the monomer orbitals causes that

$$\sum_{a'}(a|\hat{F}_A|a')S_{a'b} =\epsilon_a\,S_{ab}. \tag{14}$$

For non-canonical Hartree-Fock orbitals, e.g. localized ones, the relation

$$\sum_{a'}(a|\hat{F}_A|a')S_{a'b} =(a|\hat{F}_A|b), \tag{15}$$

holds under the conditions mentioned above. Thus, the exchange-repulsion energy in eq. (12) can be split up into contributions as follows

$$E_{\mathrm{xr}}^{P^2} = E_{\mathrm{xi}} + E_{\mathrm{xr2}} + E_{\mathrm{xr3}} + E_{\mathrm{xr4}} + E_{\mathrm{xrb}}, \tag{16}$$

with

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$$E_{\text{xr2}} = -2\sum_{ab} S_{ba}(a|\hat{F}_A + \hat{F}_B - 2\hat{T}|b) \tag{17}$$

$$E_{\text{xr3}} = 2\sum_{aa'b} S_{ba}(a|\hat{F}_B - \hat{T}|a')S_{a'b} + 2\sum_{abb'} S_{ab}(b|\hat{F}_A - \hat{T}|b')S_{b'a} \tag{18}$$

$$E_{\text{xr4}} = 2\sum_{aa'bb'} S_{ab}\Big[4(ab|a'b') - (ab'|a'b) - (aa'|bb')\Big]S_{b'a'}. \tag{19}$$

$$E_{\text{xrb}} = 2\sum_{ab} S_{ba}\left[-(a|\hat{F}_A|b) + \sum_{a'}(a|\hat{F}_A|a')S_{a'b} - (b|\hat{F}_B|a) + \sum_{b'}(b|\hat{F}_B|b')S_{b'a}\right] \tag{20}$$

In the following, we shall designate these contributions as two-index (E_{xr2}), three-index (E_{xr3}), and four-index (E_{xr4}) terms of the exchange-repulsion energy as well as its basis-set error (E_{xrb}).

The only contribution to E_{xr} with a nonzero kinetic energy contribution in Eq. (16) is E_{xrb}. As noted before, it becomes zero in the limit of a complete basis set[53,57] or if the monomer orbitals are determined in the basis set of the dimer system.[58] The remaining contributions to E_{xr} (E_{xi}, E_{xr2}, E_{xr3}, and E_{xr4}) are exclusively due to the potential energy. This explains why it is possible to obtain a correct expression for the exchange-repulsion energy that does not contain kinetic energy contributions.

All expressions for the exchange-repulsion energy and its contributions presented above are invariant with respect to unitary transformations of the orbitals on the individual systems. The terms are of the form $\sum_{ab} F_{ab}S_{ba}$ where the sum over a and b runs over all occupied orbitals on the systems A and B, respectively. As the orbital spaces of the systems are not changed by unitary transformations, the sums are also not affected. A more detailed proof of unitary invariance of $E_{\text{xr}}^{P^2}$ is given in the supporting information of this article.

As we shall see below, the terms with the largest absolute values are E_{xr2} and E_{xi}. Both contain only two orbital indices which allows defining unambiguous orbital contributions with one orbital (a) from system A and another one (b) from B. E_{xr3} and E_{xr4} cannot be unambiguously assigned to orbital pairs as they contain sums over further orbitals. However, we shall show below that E_{xr3} is rather small for neutral systems, while E_{xr4} turns out to be essentially proportional to E_{xr2}. This motivates the definition of orbital contributions to $E_{\text{xr}}^{P^2}$ which run over all occupied orbitals of the interacting systems and sum up to the exchange-repulsion energy as

$$E_{\text{xr}}^{P^2} = \sum_{ab} E_{\text{xr}}(a,b). \tag{21}$$

We designate the $E_{\text{xr}}(a,b)$ terms as Molecular-Orbital-Pair Contributions to the Exchange-repulsion energy (MOPCE). They can be partitioned in analogy to Eq. (16) as

$$E_{\text{xr}}(a,b) = E_{\text{xi}}(a,b) + E_{\text{xr2}}(a,b) + E_{\text{xr3}}(a,b) + E_{\text{xr4}}(a,b) + E_{\text{xrb}}(a,b), \tag{22}$$

with

$$E_{\text{xi}}(a,b) = -2(ab|ba), \tag{23}$$

$$E_{\text{xr2}}(a,b) = -2S_{ba}(a|\hat{F}_A + \hat{F}_B - 2\hat{T}|b), \tag{24}$$

$$E_{\text{xr3}}(a,b) = +2S_{ab}\left[\sum_{a'}(a|\hat{F}_B - \hat{T}|a')S_{a'b} + \sum_{b'}(b|\hat{F}_A - \hat{T}|b')S_{b'a}\right], \tag{25}$$

$$E_{\text{xr4}}(a,b) = +2S_{ab}\sum_{a'b'}\Big[4(ab|a'b') - (ab'|a'b) - (aa'|bb')\Big]S_{a'b'}, \tag{26}$$

$$E_{\text{xrb}}(a,b) = +2S_{ab}\left[-(a|\hat{F}_A|b) + \sum_{a'}(a|\hat{F}_A|a')S_{a'b} - (b|\hat{F}_B|a) + \sum_{b'} S_{ab'}(b'|\hat{F}_B|b)\right]. \tag{27}$$

III. EXCHANGE-REPULSION IN THE TRIPLET HYDROGEN SYSTEM

For the H_2 molecule in the $^3\Sigma_u^+$ $(1\sigma_g 1\sigma_u)$ state, the ground-state wave functions of the monomer systems and all required integrals are known analytically.[59,64,79,80]

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Furthermore, a highly accurate potential energy curve of this state is available from the seminal work of Kołos and Wolniewicz[81] who obtained the binding energy of $1.97 \times 10^{-5}\,\mathrm{E_h}$ ($\approx -0.052\,\mathrm{kJ\,mol^{-1}}$) at the interatomic distance $R = 7.8\,\mathrm{au}$ ($\approx 4.13\,\mathrm{\AA}$).

We consider a Slater determinant with two triplet-coupled electrons in the symmetrized and orthonormalized orbitals

$$1\sigma_g = \frac{1}{\sqrt{2(1+S)}}(\chi_a + \chi_b), \tag{28}$$

$$1\sigma_u = \frac{1}{\sqrt{2(1-S)}}(\chi_a - \chi_b), \tag{29}$$

resulting from the hydrogen 1s orbitals χ_a and χ_b. The corresponding energy expectation value is given by[63]

$$E = \frac{h_{aa} + h_{bb} - 2Sh_{ab} + (aa|bb) - (ab|ba)}{1 - S^2} + \frac{1}{R}. \tag{30}$$

Here $S = (\chi_a|\chi_b)$ is the overlap integral, $(ab|ba) = (\chi_a(1)\chi_b(1)|\frac{1}{r_{12}}|\chi_b(2)\chi_a(2))$ the exchange integral, and $h_{ab} = (\chi_a|\hat{h}|\chi_b)$ the one particle integral where $\hat{h} = \hat{T} + \hat{V}_A + \hat{V}_B$. We define the electrostatic energy as before by

$$E_{el} = \frac{1}{R} + (a|\hat{V}_B|a) + (b|\hat{V}_A|b) + (aa|bb). \tag{31}$$

The total energy in Eq. (30) furthermore comprises the energies of the monomers ($E_A{=}E_B$) and the exchange-repulsion energy. If we neglect all terms with higher than second order in the overlap, we obtain in analogy to the considerations above

$$\begin{aligned} E_{\mathrm{xr}}^{P^2} &= E - E_A - E_B - E_{el}. \\ &= -2h_{ab}S + [h_{aa} + h_{bb} + (aa|bb) - (ab|ba)]S^2. \end{aligned} \tag{32}$$

The contributions of the kinetic and potential energy operators to this exchange-repulsion energy are given by

$$T_{\mathrm{xr}}^{P^2} = -2T_{ab}S + (T_{aa} + T_{bb})S^2, \tag{33}$$

and

$$V_{\mathrm{xr}}^{P^2} = -2V_{ab}S + \Big[V_{aa} + V_{bb} + (aa|bb) - (ab|ba)\Big]S^2, \tag{34}$$

where $\hat{V} = \hat{V}_A + \hat{V}_B$.

In order to rewrite this result in a form that resembles the orbital contributions to the two-, three-, and four-index terms of the exchange-repulsion energy, we introduce Fock operators as e.g. $\hat{F}_A = \hat{T} + \hat{V}_A + \hat{J}_A - \hat{K}_A$. The monomer orbital χ_a is an exact eigenfunction of this operator and the respective eigenvalue is simultaneously the orbital energy and the total energy of the hydrogen atom A

$$\hat{F}_A \chi_a = E_A \chi_a. \tag{35}$$

In analogy to Eqs. (16) to (20) the approximate exchange-repulsion energy of the triplet-hydrogen system can be written as

$$E_{\mathrm{xr}}^{P^2} = E_{\mathrm{xi}} + E_{\mathrm{xr2}} + E_{\mathrm{xr3}} + E_{\mathrm{xr4}} + E_{\mathrm{xrb}}, \tag{36}$$

with

$$E_{\mathrm{xi}} = -(ab|ba) \tag{37}$$

$$E_{\mathrm{xr2}} = -(a|\hat{F}_A + \hat{F}_B - 2\hat{T}|b)S \tag{38}$$

$$E_{\mathrm{xr3}} = +S^2\Big[(b|\hat{F}_A - \hat{T}|b) + (a|\hat{F}_B - \hat{T}|a)\Big] \tag{39}$$

$$E_{\mathrm{xr4}} = -S^2\Big[(aa|bb) - (ab|ba)\Big] \tag{40}$$

$$E_{\mathrm{xrb}} = S[-(a|\hat{F}_A|b) + (a|\hat{F}_A|a)S] - (b|\hat{F}_B|a) + (b|\hat{F}_B|b)S]] \tag{41}$$

The contributions to $E_{\mathrm{xr}}^{P^2}$ for the (open-shell) triplet hydrogen system are written here in a form corresponding to the closed-shell-singlet interactions of Eqs. (7), (17), (18), and (19). The basis-set error E_{xrb} is zero, as the wave functions are exact eigenfunctions of the Fock operators, and therefore neglected. We note, that the kinetic energy contribution to the exchange-repulsion energy is completely contained in this term. The two index term can be rewritten as

$$E_{\mathrm{xr2}} = -(b|a)(a|\hat{V}_B|b) - (a|b)(b|\hat{V}_A|a). \tag{42}$$

As the electron-nuclear attraction operators $\hat{V}_A$ and $\hat{V}_B$ are strictly negative, E_{xr2} is a positive quantity. Similarly, the three index term E_{xr3} can also be expressed as a matrix element containing exclusively potential energy operators

$$E_{\mathrm{xr3}} = S^2\Big[(b|\hat{V}_A + \hat{J}_A - \hat{K}_A|b) + (a|\hat{V}_B + \hat{J}_B - \hat{K}_B|a)\Big]. \tag{43}$$

For the hydrogen 1s ground state atomic orbitals, the matrix elements discussed in the preceding subsection are analytically known and collected in the appendix. With these expressions, the asymptotically leading terms of the exchange-repulsion energy contributions can be written as polynomials of the interatomic distance R times a power of e^{-2R} as

$$E_{\mathrm{xr2}} = \left(2 + 4R + \frac{8}{3}R^2 + \frac{2}{3}R^3\right)e^{-2R} \tag{44}$$

$$E_{\mathrm{xr3}} = -\left(\frac{R^6}{27} + \mathcal{O}(R^5)\right)e^{-4R} \tag{45}$$

$$E_{\mathrm{xr4}} = -\left(\frac{1}{R} + 2 + \frac{5}{3}R + \frac{2}{3}R^2 + \frac{1}{9}R^3\right)e^{-2R}. \tag{46}$$

E_{xr3} is generally negative but small as compared with the two and four index terms which are positive and negative, respectively. For large R the ratio $E_{\mathrm{xr4}}/E_{\mathrm{xr2}}$ approaches $-\frac{1}{6}$.

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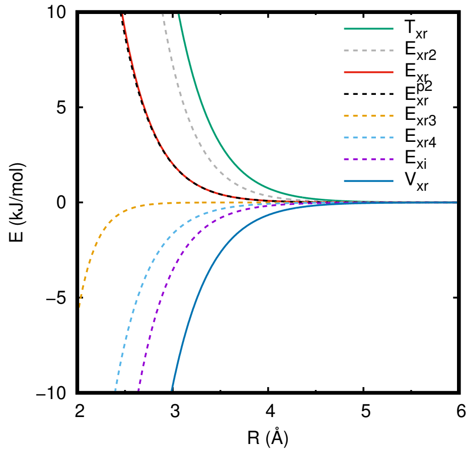

FIG. 1. Exchange-repulsion energy and its contributions for the ${}^3\Sigma_u^+$ $(1\sigma_g 1\sigma_u)$ state of H_2 as a function of the interatomic distance R.

TABLE I. E_{xr} and its contributions as well as the electrostatic energy of the ${}^3\Sigma_u^+$ state of the H_2 molecule. Relative energies as compared to the exchange-repulsion energies are also shown to indicate to which extent the energy contributions are proportional to E_{xr}. Energies are given in kJ mol^{-1}.

r (au)	5.2		7.8	
r (Å)	2.75		4.13	
	E	E/E_{xr}	E	E/E_{xr}
E_{xr}	4.30	1	0.057 80	1
T_{xr}	21.91	5.10	0.519 89	8.99
V_{xr}	−17.70	−4.12	−0.462 11	−7.99
$E_{\mathrm{xr}}^{P^2}$	4.22	0.98	0.057 78	1.00[b]
E_{xr2}	15.07	3.50	0.225 59	3.90
E_{xr3}	−0.11	−0.02	−0.000 04	0.00
E_{xr4}	−3.50	−0.81	−0.047 77	−0.83
E_{xi}	−7.24	−1.68	−0.120 01	−2.08
E_{int}[a]	2.43	0.57	−0.051 72	−0.89

[a] after Kołos and Wolniewicz.[81]

[b] with more digits this value is 0.9997.

The corresponding expansion of the kinetic energy contribution to the exchange-repulsion energy of Eq. (33) is

$$T_{\mathrm{xr}}^{P^2} = \left(\frac{2}{3}R^2 + \frac{2}{3}R^3 + \frac{2}{9}R^4\right) e^{-2R}. \qquad (47)$$

We see that $T_{\mathrm{xr}}^{P^2}$ decays as $R^4\, e^{-2R}$ for large R, whereas the repulsion energy contributions behave as $R^3\, e^{-2R}$. For that reason, we may conclude that the kinetic energy contribution, T_{xr}, is less appropriate to describe the repulsive interaction than E_{xr2} and E_{xr4}.

It is known[63,82–84] that the Heitler-London Ansatz[59] for the exchange-repulsion energy used here becomes inadequate for large distances. Herring and Flicker[83] as well as Smirnov and Chibisov[84] derived that the correct asymptotic behavior of the exchange-repulsion energy of the H_2 triplet state is proportional to $R^{2.5}e^{-2R}$ while the Heitler-London analog behaves as $-R^3\ln(R)e^{-2R}$ due to a respective term in E_{xi}. However, as pointed out by Tang *et al.* in Ref. 80 the present approximation is reasonable for inter-atomic distances where the exchange-repulsion energy is in the order of the thermal energy at room temperature.

In Fig. 1 E_{xr} and its contributions are depicted as a function of the interatomic distance R. The figure underlines that the kinetic and potential energy contributions are positive and negative, respectively, and their absolute values are both significantly larger than the exchange-repulsion energy itself. E_{xr2} is positive and larger than E_{xr}, while the other contributions of the exchange-repulsion energy are consistently negative. As expected from the asymptotic expansions of the contributions to E_{xr} in Eqs. (44–46), E_{xr3} is much smaller in absolute value than the exchange-repulsion energy and the other contributions to it. The four index term E_{xr4} is negative and about of the same absolute size as E_{xr} while E_{xi} is even more negative.

Further insight into the behavior of the contributions to the exchange-repulsion energy of the H_2 (${}^3\Sigma_u^+$) system is provided in Table I where the numerical values of these energies are collected for two structures. At $R = 5.2$ au the very accurate Born-Oppenheimer potential energies of Kołos and Wolniewicz[81] correspond to the average thermal energy at 292 K (i.e. about room temperature), while the minimum of the respective potential energy curve is found at the other structure with $R = 7.8$ au. At the minimum E_{xr} is approximately the negative of E_{int}, indicating that here the attractive contributions to the interaction energy are about minus two times the exchange-repulsion energy. $E_{\mathrm{xr}}^{P^2}$ underestimates E_{xr} by only 0.03 % (1.9 %) for $R = 7.8$ au (5.2 au). At these distances, the kinetic energy grossly exceeds E_{xr} by a factor of 5 (9). The contributions E_{xr2}, E_{xr3}, E_{xr4}, and E_{xi} are essentially proportional to E_{xr}.

In the following, we want to investigate the exchange-repulsion energy of a given aggregate system for structures that can be considered to be chemically relevant. For decreasing distances between the constituent components, E_{xr} increases exponentially, soon becoming so large that the respective structures can hardly be reached in a thermal ensemble. We tentatively define the upper limit for chemically relevant exchange-repulsion energies as the highest E_{xr} value found for an aggregate structure which has an intermolecular energy that is 12 kJ/mol above the minimum structure. According to the Boltzmann distribution, this short-distance aggregate structure is populated at 298 K for about 100 times less likely than the equilibrium structure. With increasing distance, the exchange-repulsion energy decreases and soon reaches such small values that it does not influence the population of aggregate structures any more. The definition of the lower boundary for chemically relevant exchange-repulsion energies is less clear, as we have to distinguish whether the aggregate is dissociating due to thermal acti-

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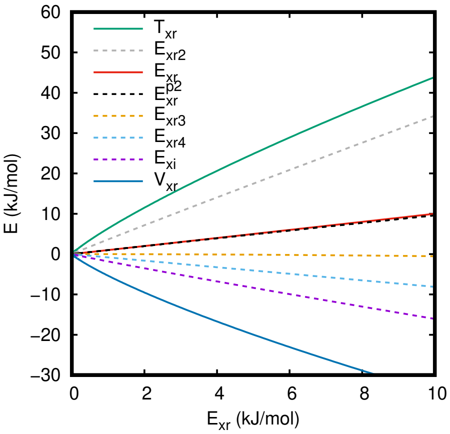

FIG. 2. Exchange-repulsion energy and its contributions for the $^3\Sigma_u^+$ $(1\sigma_g 1\sigma_u)$ state of the H_2 molecule as a function of E_{xr}.

vation or not. The former case is assumed to be reached when the dissociation energy of the aggregate is below 10 kJ/mol. In this case, the aggregate is rather weakly bound and we define the lower bound to be the exchange-repulsion energy of the equilibrium structure. For higher aggregate binding energies the lower boundary is set to the lowest E_{xr} value found for a long-distance aggregate whose interaction energy is 12 kJ/mol above the equilibium energy. According to Tab. I the chemically relevant E_{xr} values for the H_2 ($^3\Sigma_u^+$) system are thus in the range between 10 kJ/mol and 0.05 kJ/mol.

Fig. 2 shows the contributions of the exchange-repulsion energy as a function of E_{xr} in the chemically relevant region. E_{xr2}, E_{xr3}, E_{xr4}, and E_{xi} can be well represented with zero point straight lines with slopes of 3.4, −0.04, −0.8, and −1.7, respectively. Thus, the exchange-repulsion energy is essentially proportional to E_{xr2}, E_{xr4}, and E_{xi} and may be obtained from this property.

Further insight is provided from Fig. 2 where the contributions to the exchange-repulsion energy are plotted as a function of E_{xr} itself. While a simple functional relation between T_{xr} or V_{xr} and E_{xr} does not exist, E_{xr2}, E_{xr4}, and E_{xi} are in reasonable approximation proportional to E_{xr}. The positive value of the exchange-repulsion energy is clearly due to E_{xr2} as E_{xr3}, E_{xr4} and E_{xi} are (at least for the present case) strictly negative.

IV. INTERPRETATION OF THE CONTRIBUTIONS TO THE EXCHANGE-REPULSION ENERGY

In this section, we discuss different forms of the contributions to the exchange-repulsion energy and suggest how they can be interpreted. As derived above, E_{xr2} can be written as

$$E_{\mathrm{xr2}} = -\sum_{a,b} 2S_{ba}\Big[(\epsilon_a + \epsilon_b)S_{ab} - 2T_{ab}\Big] \tag{48}$$

$$= -\sum_{a,b}\Big[2S_{ab}(b|\hat{V}_A + 2\hat{J}_A - \hat{K}_A|a) + 2S_{ba}(a|\hat{V}_B + 2\hat{J}_B - \hat{K}_B|b)\Big] \tag{49}$$

$$= -\sum_a 2\left(a\left|\sum_b |b)(b| \quad \hat{V}_A + 2\hat{J}_A - \hat{K}_A\right|a\right) - \sum_b 2\left(b\left|\sum_a |a)(a| \quad \hat{V}_B + 2\hat{J}_B - \hat{K}_B\right|b\right). \tag{50}$$

Here, Eq. (48) is particularly interesting for a numerical implementation as it contains only one-electron matrix elements which are easily available if the orbitals and the orbital energies are known.

Eqs.(49) and (50) show that E_{xr2} can be written as a pure potential energy contribution. In contrast to E_{xr3}, E_{xr4}, and E_{xi}, which are generally negative, it is the only significant positive contribution to E_{xr}. Thus, E_{xr2} is the central ingredient of the Pauli repulsion. The latter is a consequence of the Pauli principle, which enforces that two electrons with like spin must not occupy the same spatial region. This can be related to Eq. (50) as follows: In bound electronic states, the electrons must be more strongly attracted by the nuclei than repelled by other electrons. Due to Pauli repulsion, a part of this attraction is erased as follows: The right-hand part of the first term in Eq. (50) at the position $\vec{r}$, $|\hat{V}_A + 2\hat{J}_A - \hat{K}_A|\psi_a(\vec{r}))$, is the potential energy of an electron in orbital ψ_a due to the field of the nuclei and the other electrons in the system A in the Hartree-Fock approximation. The exchange operator $\hat{K}_A$ in that expression erases the interaction of the electron in orbital ψ_a with itself as $|\hat{J}_a - \hat{K}_a|a) = 0$. The left-hand part of the same matrix element, $(a|\sum_b |b)(b|$, is the projection of the electron in the spatial orbital ψ_a upon the occupied orbitals in system B. The prefactor -2 results from the fact that the electron density of the projected orbital is Pauli forbidden and thus not existent (minus sign) in the orbital ψ_a which is occupied by two electrons (factor two). The second term in Eq. (50) represents the same for the electrons on the system B. In other words, E_{xr2} accounts for the reduced attraction of the electrons within system A due to the fact that these electrons cannot be at the same place as those from system B and vice versa.

This interpretation of E_{xr2} resembles earlier work by Salem,[49] where the exchange-repulsion energy was derived from Hellmann-Feynman forces. However, while Salem proposed that only the electron nuclear attraction is responsible for the repulsive interaction, our results indicate that the repulsion of the electrons also has to be considered.

We note that E_{xr2} is reminiscent to the exchange-repulsion energy contributions discussed by Rackers and Ponder.[85] These authors argued that the Pauli exclu-

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sion principle generates “holes” in the electron density at places where two orbitals of different molecules overlap. These holes can be interpreted as positive charge densities that are interacting with the electrostatic potential of the two molecules. Indeed, both terms can be seen as the interaction between the electrostatic potential of one system with non-existent electronic charge due to the Pauli-exclusion principle. The three-index term evaluates the interaction of the charge density generated by the overlap of a given orbital of system A with all orbitals of B with the potential energy that electrons feel at A and vice versa.

The three-index term E_{xr3} can be written as

$$E_{\mathrm{xr3}} = 2\Bigg[\sum_b \Bigg(b\Bigg| \sum_a |a)(a| \quad \hat{V}_B + 2\hat{J}_B - \hat{K}_B \sum_{a'} |a')(a'| \Bigg| b\Bigg) + \sum_a \Bigg(a\Bigg| \sum_b |b)(b| \quad \hat{V}_A + 2\hat{J}_A - \hat{K}_A \sum_{b'} |b')(b'| \Bigg| a\Bigg)\Bigg]. \tag{51}$$

This may be considered to avoid double counting of contributions to the two-index term, which are forbidden by the Pauli exclusion principle. E_{xr4} is the result of an electron-repulsion interaction and can be interpreted as a very similar correction, which avoids double counting of contributions to the electron-electron interaction in E_{xr2}.

E_{xi} is a common exchange integral that exists also if all orbitals are orthogonal, as e.g. in the energy expression of the monomers in Eq. (3). This term is always negative and generally of comparable absolute size as the exchange-repulsion energy. It may be interpreted as a correction to the electron-electron repulsion for that part of the electronic density that does not exist due to the Pauli principle.

V. IMPLEMENTATION

We implemented the P^2 and S^2 approximations to the exchange-repulsion energy and the respective orbital contributions in our local quantum chemistry package “wavels”[86–90] in two independent forms. One of them transforms the integrals of the kinetic-energy, electron-nuclear attraction and the electron-repulsion operators to the basis sets of the Hartree-Fock orbitals of the considered systems and evaluates the Heitler-London exchange-repulsion following Eq. (5), the $E_{\mathrm{xr}}^{P^2}$ and $E_{\mathrm{xr}}^{S^2}$ approximations (according to Eqs. (10) and (11) as well as the orbital contributions to $E_{\mathrm{xr}}^{P^2}$ [Eqs. (7) and (17-19)].

A more efficient evaluation of $E_{\mathrm{xr}}^{P^2}$ was implemented as follows. The symmetric density matrices $\mathbf{D}^A$ and $\mathbf{D}^B$ of the monomers are evaluated according to e.g. $D^A_{\mu\nu} = \sum_a 2c_{\mu a}c_{\nu a}$, with the MO expansion coefficients $c_{\mu a}$. Fock-type two electron operators

$$G_{\lambda\sigma}(\mathbf{D}) = \sum_{\mu\nu} D_{\mu\nu}\left[2(\mu\nu|\lambda\sigma) - (\lambda\nu|\mu\sigma)\right] \tag{52}$$

are determined for these densities as well as for the symmetric overlap density

$$D^S_{\mu\nu} = \sum_{ab} S_{ab}\left(c_{\mu a}c_{\nu b} + c_{\nu a}c_{\mu b}\right). \tag{53}$$

Transformation of these operators, the overlap matrix, the kinetic energy and the electron-nuclear attraction operators to the MO basis provides the orbital contributions to the exchange-repulsion energy contributions via

$$E_{\mathrm{xr2}}(a,b) = 2S_{ab}\left[V_{A,ab} + G_{ab}(\mathbf{D}^A) + V_{B,ab} + G_{ab}(\mathbf{D}^B)\right] S_{ab} \tag{54}$$

$$E_{\mathrm{xr3}}(a,b) = 2S_{ab}\Bigg\{\sum_{a'}\left[V_{B,aa'} + G_{aa'}(\mathbf{D}^B)\right] S_{a'b} + \sum_{a'}\left[V_{A,bb'} + G_{bb'}(\mathbf{D}^A)\right] S_{ab'}\Bigg\} \tag{55}$$

$$E_{\mathrm{xr4}}(a,b) = 2S_{ab}G_{ab}(\mathbf{D}^S), \tag{56}$$

where e.g. $V_{A,ab} = \sum_{\mu\nu} c_{\mu a}(\mu|\hat{V}_A|\nu)c_{\nu b}$. While three Fock-type two electron operators are required for the two, three, and four index contributions to the exchange-repulsion energy, the exchange-integral contribution requires evaluating an exchange operator

$$E_{\mathrm{xi}} = \sum_a K_{aa}(\mathbf{D}^B), \tag{57}$$

or several of them if individual orbital contributions, $E_{\mathrm{xr}}(a,b)$ are desired.

The two implementations provide identical E_{xr} energy values within numerical accuracy (1 nE$_\mathrm{h}$). Furthermore, the exchange energies evaluated by Söderhjelm *et al.*[46] for the 1401 water-water dimer structures with the cc-pVDZ basis (and without a ghost-basis) agree with our $E_{\mathrm{xr}}^{S^2}$ values with an average error of about 2 µE$_\mathrm{h}$.

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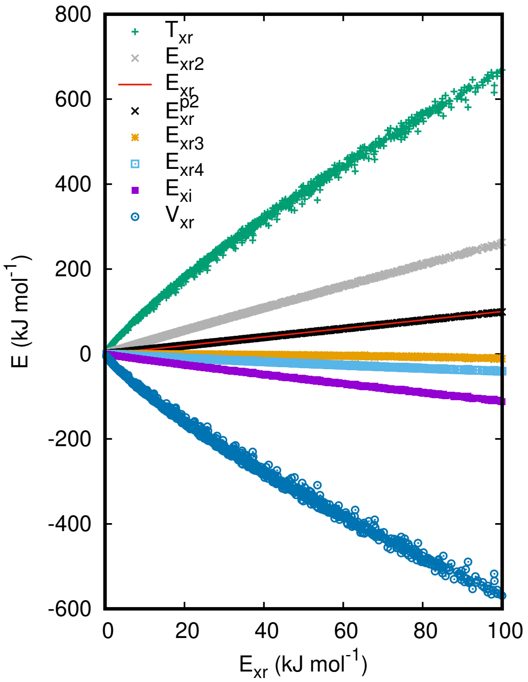

FIG. 3. Contributions to the exchange-repulsion energy and its P^2 approximation as a function of the exchange-repulsion energy as evaluated for the 1401 water-water structures from the collection of Söderhjelm, Karlström and Ryde.[46]

VI. BEHAVIOR OF EXCHANGE-REPULSION ENERGY CONTRIBUTIONS FOR CLOSED SHELL SYSTEMS

To gain insight into the relative size, the order of magnitude, and the characteristic behavior of the contributions to the exchange-repulsion energy for the interaction of closed shell molecules we consider the water dimer in the structures collected by Söderhjelm, Karlström and Ryde[46] and from the S22x5 set of Gráfová *et al.*[91] Furthermore we present results for stationary points of the $N_2 \cdots Ar$[92,93] and $Cl_2 \cdots Ar$ systems[94–96] which are experimentally and theoretically well established.

Fig. 3 shows the calculated values for $E_{\text{xr}}^{P^2}$ and its contributions as a function of the related E_{xr}-value for the 1401 structures compiled by Söderhjelm *et al.*[46] The data were obtained with the aug-cc-pVTZ basis set.[97,98] The Boys-Bernardi type ghost basis[78] was consistently used to represent the monomer orbitals. Further increase of the basis set did not show significant changes of the results. The figure shows the chemically relevant E_{xr} range of the water dimer which can be deduced from Tab. II to be the range between 100 kJ/mol and 1 kJ/mol. Similar to the triplet H_2-system, the contributions to $E_{\text{xr}}^{P^2}$ are in a good approximation proportional to E_{xr} with proportionality constants of 2.61, −0.07, −0.42, and −1.13 for E_{xr2}, E_{xr3}, E_{xr4}, and E_{xi}, respectively. While the trend of these relations is very similar to the observations on the triplet H_2-system, the absolute values of the proportionality constants of the water dimer structures are smaller with the exception of E_{xr3}. In the water dimer the latter deviates slightly but clearly from zero, while it is essentially negligible for the triplet H_2 system with its neutral and non-polar monomers. This identifies E_{xr3} as a correction for the double counting of two-index terms, which are forbidden by the Pauli exclusion principle. For all cases considered here, E_{xr3} is by far the smallest contribution to the exchange-repulsion energy. While E_{xr2}, E_{xr4}, and E_{xi} seem to be essentially proportional to E_{xr}, the kinetic- and potential-energy contributions to the exchange-repulsion energy are much less well related to this target property.

Contributions to the exchange-repulsion energy for the T-shaped and linear stationary points of the $N_2 \cdots Ar$ and the $Cl_2 \cdots Ar$ systems, as well as the five water dimer structures from the S22x5 set, are collected in Tab. II. As discussed above, the exchange-repulsion energies are of the same order of magnitude or even larger than the absolute interaction energies for the equilibrium structures or arrangements with shorter distance. As these arrangements are of crucial importance for the properties of aggregates, it is clear that the total interaction energy, E_{int}, can be hardly rationalized without understanding E_{xr}. The kinetic energy contribution exceeds E_{xr} by factors between 7 and 18 in a seemingly arbitrary fashion. While the kinetic energy contribution of E_{xr} is always positive, the potential energy contribution, V_{xr}, is a large negative number. $E_{\text{xr}}^{P^2}$ is an excellent approximation to E_{xr}, in particular if the distance between the systems is larger than the equilibrium distance. However, even for the compressed 0.9 r_e structure of the water dimer, the error amounts only to 0.4 kJ mol^{-1} or 0.7 % where $E_{\text{xr}}^{P^2}$ is consistently smaller than E_{xr}. While E_{xr} and E_{xr2} are always positive, E_{xr4} and E_{xi} are consistently negative. E_{xr3} has generally negative values but as we found for about 2.5 % of the 1401 water dimer structures of Söderhjelm *et al.*,[46] it can be slightly positive. The maximum value found was however only about +0.09 kJ mol^{-1} while the most negative value is in the order of −30 kJ mol^{-1}.

Tab. II also shows SAPT exchange energies in the perturbation order $E_{\text{exch}}^{(1,0)}$ and $E_{\text{exch}}^{(1,2)}$ generally designated as SAPT0 and SAPT2, respectively. The difference between these levels is a measure for the error of the exchange-repulsion energies. It is typically in the order of 10 % and larger than the deviation of the $E_{\text{xr}}^{P^2}$ or the $E_{\text{xr}}^{S^2}$ approximations from E_{xr}. For that reason, the approximations inherent in these methods are moderate, and it can be expected that they reproduce essential features of the exchange-repulsion energy. Similarly, the two index term, E_{xr2}, overestimates the exchange-repulsion energy by about a factor of three. As this is within the accuracy of E_{xr}, the exchange-repulsion energy may be estimated from this term. The same is not possible for the three index term, which is even changing sign, as seen for dif-

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TABLE II. Exchange-repulsion energy and its contributions as well as SAPT data for stationary points on the $Cl_2\cdots Ar$ and $N_2\cdots Ar$ dimers as well as five points of the water dimer structure. All results were obtained with the aug-cc-pVTZ basis including a ghost-basis for the monomers. All energies in $\mathrm{kJ\,mol^{-1}}$.

	$Cl_2\cdots Ar$		$N_2\cdots Ar$				water dimer		
	linear	T-shape	linear	T-shape	0.9 r_e	1.0 r_e	1.2 r_e	1.5 r_e	2.0 r_e
E_{int}	-2.61[a]	-2.62[a]	-0.97[b]	-1.27[b]	-18.14[c]	-20.89[c]	-16.99[c]	-9.64[c]	-4.04[c]
E_{xr}	3.73	3.41	1.03	1.67	60.24	29.70	7.12	0.82	0.02
T_{xr}	58.57	57.94	17.85	25.48	442.82	248.85	75.55	11.72	0.46
V_{xr}	-54.84	-54.53	-16.83	-23.81	-382.58	-219.15	-68.43	-10.90	-0.44
$E_{\mathrm{xr}}^{S^2}$	3.72	3.40	1.03	1.67	-103.68	-58.27	-17.66	-2.72	-0.11
$E_{\mathrm{xr}}^{P^2}$	3.73	3.41	1.03	1.67	59.83	29.57	7.11	0.82	0.02
E_{xr2}	11.15	10.80	3.19	5.10	160.79	81.59	20.64	2.55	0.07
E_{xr3}	-0.11	0.01	0.01	-0.01	-4.60	-1.44	-0.15	-0.01	-0.00
E_{xrb}	0.00	0.00	0.00	-0.00	0.00	0.00	0.00	-0.00	-0.00
E_{xr4}	-1.84	-1.89	-0.59	-0.91	-26.34	-13.89	-3.59	-0.44	-0.01
E_{xi}	-5.47	-5.50	-1.58	-2.51	-70.02	-36.68	-9.79	-1.29	-0.04
$T_{\mathrm{xr}}/E_{\mathrm{xr}}$	15.70	16.99	17.39	15.24	7.35	8.38	10.61	14.29	21.17
$E_{\mathrm{xr}}^{P^2}/E_{\mathrm{xr}}$	1.00	1.00	1.00	1.00	0.99	1.00	1.00	1.00	1.00
$E_{\mathrm{xr2}}/E_{\mathrm{xr}}$	2.99	3.16	3.10	3.05	2.67	2.75	2.90	3.11	3.47
$E_{\mathrm{xr3}}/E_{\mathrm{xr}}$	-0.03	0.00	0.01	-0.01	-0.08	-0.05	-0.02	-0.01	-0.00
$E_{\mathrm{xrb}}/E_{\mathrm{xr}}$	0.00	0.00	0.00	-0.00	0.00	0.00	0.00	-0.00	-0.00
$E_{\mathrm{xr4}}/E_{\mathrm{xr}}$	-0.49	-0.55	-0.58	-0.54	-0.44	-0.47	-0.50	-0.53	-0.57
$E_{\mathrm{xi}}/E_{\mathrm{xr}}$	-1.46	-1.61	-1.54	-1.50	-1.16	-1.23	-1.38	-1.57	-1.89
SAPT									
E_{el}	-1.23	-1.31	-0.34	-0.47	-50.79	-34.26	-17.67	-8.48	-3.56
$E_{\mathrm{exch}}^{(1,2)}$	3.99	3.78	1.13	1.65	66.38	33.69	8.51	1.05	0.03
$E_{\mathrm{exch}}^{(1,0)}$	3.70	3.39	1.02	1.66	58.76	29.13	7.02	0.81	0.02
$E_{\mathrm{exch}}^{(1,0)}(S^2)$	3.70	3.39	1.02	1.66	57.99	28.92	7.01	0.81	0.02
E_{ind}	-0.73	-0.20	-0.06	-0.06	-18.89	-10.15	-3.21	-0.72	-0.11
E_{disp}	-4.79	-4.96	-1.75	-2.43	-13.18	-8.63	-3.85	-1.26	-0.26
$E_{\mathrm{int}}(\mathrm{SAPT0})$	-2.85	-2.85	-1.04	-1.28	-22.49	-23.33	-18.03	-10.16	-4.24
$E_{\mathrm{int}}(\mathrm{SAPT2})$	-2.75	-2.70	-1.01	-1.31	-16.47	-19.35	-16.22	-9.40	-3.90

[a] According to Nunzi *et al.* [94]
[b] According to Candori *et al.* [92]
[c] According to Gráfová *et al.* [91]

ferent arrangements of the $Cl_2\cdots Ar$ and the $N_2\cdots Ar$ systems. The four index term correlates quite well with E_{xr}. The ratio between the exchange integral and the exchange-repulsion energy varies a bit more than those for the two- and four-index terms. We conclude that E_{xr2} seems be a reasonable measure of E_{xr}.

We demonstrated that it is possible to split $E_{\mathrm{xr}}^{P^2}$ into contributions with a physical meaning: On the one hand the two-, three-, four-index terms as well as the exchange integral and on the other hand the orbital contributions, $E_{\mathrm{xr}}(a,b)$ were identified. Both options provide valuable tools for getting a reliable and comprehensible insight into this important contribution to noncovalent interaction energies.

VII. CONCLUSIONS

A reliable approximation to the exchange-repulsion energy termed $E_{\mathrm{xr}}^{P^2}$ is derived from the energy expectation value of interacting systems in their Hartree-Fock representations (Heitler-London approach)[59] which is essentially equivalent to the symmetry adapted perturbation theory (SAPT) expression. Kinetic and potential energy contributions of the former exchange-repulsion energy are defined in accordance with a proposal of Baerends.[2] These contributions happen to be positive and negative, respectively. While this supports the designation of E_{xr} as kinetic repulsion, the asymptotic behavior of T_{xr} and E_{xr} are different and the correlation between these contributions to the interaction energy is poor.

We demonstrate that $E_{\mathrm{xr}}^{P^2}$ is essentially equivalent to the SAPT0 exchange energy and its S^2 approximate termed SAPT(S^2) whose kinetic energy contributions are exactly zero. We show that $E_{\mathrm{xr}}^{P^2}$ contains a basis set dependent contribution, E_{xrb}, which includes the complete kinetic energy contribution of E_{xr} but vanishes if the monomers are represented with correct Hartree-Fock wave functions or with a Boys-Bernardi type[78] "ghost" basis. This term is neglected in SAPT, which explains that a reliable representation of the exchange-repulsion energy does nor require kinetic energy contributions. Without the basis-set dependent contribution, $E_{\mathrm{xr}}^{P^2}$ is exclusively due to potential energy contributions and can be partitioned into four contributions (E_{xr2}, E_{xr3}, E_{xr4}, and E_{xi}). The dominant one, E_{xr2}, is interpreted in analogy to a former proposal of Salem[49] who argued that the Pauli principle effectively reduces electron density at places where electrons of both systems occur, causing an increase of the potential energy. In our model, this potential energy is due to the interaction of the missing electron density with the nuclei and the other electrons of the system, while Salem proposed it to be exclusively due to electron nuclear interactions. E_{xr3} is much smaller in absolute value than the other contributions to E_{xr} and generally negative. It may be interpreted as correcting an over-counting of E_{xr2}. E_{xr4} may be seen as a similar correction and turns out to be consistently negative. E_{xi} is even more negative, and represents the ordinary exchange integral contribution that also exists for orthogonal orbitals.

An important advantage of $E_{\mathrm{xr}}^{P^2}$ lies in the fact that it allows to define Molecular Orbital Pair Contributions to the Exchange-repulsion (MOPCE) energies. While this partitioning is unique for E_{xr2} and E_{xi}, it is not unambiguous for E_{xr3} and E_{xr4}. However, as the later contributions are, respectively, either rather small or in a very good approximation proportional to E_{xr2}, the partitioning is reasonable. Orbital contributions to the exchange-repulsion energy have already been used to explain the most favorable planar displaced structures of the benzene dimer as well as of the benzene-hexafluorobenzene system.[34]

We note that similar orbital considerations are the cornerstone of frontier orbital theory.[99–101] Their effect on intermolecular interactions have been considered in the Klopman-Salem model,[102,103] however, with the focus on chemical reactivity and in a more qualitative manner. Instead, the analysis of the exchange-repulsion energy, E_{xr}, presented here, gives rise to quantitative energy contributions. Thus, it provides a sound rationalization for the repulsive intermolecular interactions in terms of a well-established concept in quantum chemistry. Furthermore, our interpretation is in line with qualitative arguments on orbital contributions to repulsive interactions proposed before.[104–106] In the present work, these ideas are raised to a well-defined quantitative theory.

The contributions to $E_{\mathrm{xr}}^{P^2}$ are investigated for the H_2 molecule in the ${}^3\Sigma_u^+$ $(1\sigma_g 1\sigma_u)$ state. Here, the related monomer orbitals and integrals are known and provide analytical representations of the exchange-repulsion energy as well as its contributions. This indicates that the kinetic and potential contribution to the exchange-repulsion energy behave rather differently than E_{xr} itself, while $E_{\mathrm{xr}}^{P^2}$ and its leading contributions E_{xr2}, E_{xr4}, and E_{xi} are in good approximation proportional to E_{xr} and have a similar asymptotic behavior. Similar results are obtained for the analysis of the exchange-repulsion energy of several closed shell systems.

We conclude that it bears clear advantages to interpret the exchange-repulsion energy as a contribution of the potential energy. This is in line with the very successful SAPT approach and provides a physical picture that allows to develop for efficient approximations of the exchange-repulsion energy as shown above and in previous works.[34,49,85] While a kinetic energy contribution to the exchange-repulsion energy can be defined[2,50–52] it is less clear how it can be related to the true exchange-repulsion energy.

We believe that the possibility to gain insight into the exchange-repulsion energy will have important impact on further investigations of noncovalent interactions. Aggregate systems that are presently investigated in our laboratory indicate that the partitioning presented in this work allows obtaining novel insight into the energetics and properties of aggregates. Preliminary results show that the technologically important and biologically interesting case of π-aggregates can be modelled and understood by such an analysis. This may aid to overcome the persistent challenges[1,19,22,23,107,108] in understanding and representing the exchange-repulsion energy with a generally applicable, simple and transferable model.

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