Communication: Efficient Approximate Screening Techniques for Integrals over London Atomic Orbitals

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Abstract

Efficient integral screening techniques are essential for the investigation of extended molecular structures. This work presents a critical assessment of well-established approximate screening techniques and extends them for integrals over London atomic orbitals, which are required in the presence of strong, external magnetic fields. Through the examination of helium clusters in such extreme environments, we demonstrate that seemingly straightforward extensions of field-free screening techniques as proposed in recent literature can lead to significant errors. To rectify this, we propose an enhanced screening technique that leads to the desired speedups while still displaying a well-contained error control.

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1 Introduction

Recent years have seen a rapidly increasing amount of investigations on atoms and molecules in strong magnetic fields, such as those found in the vicinity of interstellar objects like magnetic white dwarfs.[1–3] Field strengths of up to 10^5 T may be found under these conditions, while the strongest non-destructive fields currently obtainable in laboratories are small in comparison (150 T).[4–7] As such, quantum chemical calculations are needed in order to interpret astrophysical data for these systems. This requires the inclusion of a finite magnetic field into the molecular Hamiltonian and the subsequent use of complex-valued London atomic orbitals (LAOs) in order to ensure gauge origin invariance of all observable properties.[8,9] A wide variety of quantum chemical methods has thus been adapted for the finite magnetic field approach together with the use of non-perturbative London orbitals, including Hartree-Fock (HF),[10–15] density functional theory (DFT),[16–25] coupled cluster (CC),[26–32] full configuration interaction (FCI),[1] and GW/BSE.[33–35]

Of particular interest is the determination of the molecular structure for systems in these extreme environments.[36] Recently, several studies concerned with the determination of molecular structures in strong magnetic fields have been put forward.[32,37–41] This includes investigations on exotic structures such as helium dimers or clusters bound via a novel perpendicular paramagnetic bonding mechanism that may be found in these extreme environments.[1,36,38,41,42]

The computational investigation of extended molecular systems necessitates efficient integral screening techniques, particularly for two-electron integrals over LAOs.[37,43,44] For calculations in the absence of magnetic fields, several approximate screening techniques are well-established.[45–48] In this work, we critically assess how to adapt such techniques for calculations in strong magnetic fields. Here, the mixed plane-wave / Gaussian-type orbital (PW/GTO) character of London orbitals leads to some intricacies that need to be taken into account when introducing approximate integral screening techniques. We demonstrate that seemingly straightforward approaches can lead to significant errors.[37,43] Finally, we present some approximate integral screening techniques that fulfill all requirements of their field-free counterparts and critically assess their implementations in development versions of CFOUR[49,50] and the TURBOMOLE[51–53] program suite.

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2 Screening Techniques

For self-consistent field calculations such as HF or DFT, the evaluation of two-electron integrals,

$$(\mu\nu|\kappa\lambda) = \iint \frac{\omega_\mu^*(\mathbf{r})\omega_\nu(\mathbf{r})\omega_\kappa^*(\mathbf{r}')\omega_\lambda(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}', \tag{1}$$

is generally the most time-consuming step. As previously mentioned, a LAO,[8,9]

$$|\mu) := \omega_\mu(\mathbf{r}) = e^{-\frac{i}{2}\mathbf{B}\times(\mathbf{R}^\mu-\mathbf{O})\cdot\mathbf{r}}\chi_\mu(\mathbf{r}), \tag{2}$$

has a mixed PW/GTO character, with χ_μ being a Cartesian GTO of the form

$$\chi_\mu(\mathbf{r}) = \sum_{j=1}^{N_{\mathrm{contr}}} N_{\mu j}(x-R_x^\mu)^{a_x^\mu}(y-R_y^\mu)^{a_y^\mu}(z-R_z^\mu)^{a_z^\mu}e^{-\alpha_{\mu j}(\mathbf{r}-\mathbf{R}^\mu)^2} \tag{3}$$

or, alternatively, a spherical GTO of the form

$$\chi_\mu(\mathbf{r}) = \sum_{j=1}^{N_{\mathrm{contr}}} \tilde{N}_{\mu j}Y_{l,m}(\theta,\phi)(\mathbf{r}-\mathbf{R}^\mu)^l e^{-\alpha_{\mu j}(\mathbf{r}-\mathbf{R}^\mu)^2}, \tag{4}$$

where μ,ν,κ,λ are referring to basis set indices. The GTO shown in eq. (3) or (4) is constructed as linear combination of N_{contr} primitive functions. It is centered at $\mathbf{R}^\mu$, the static, homogeneous magnetic field is given by $\mathbf{B}$ and $\mathbf{O}$ refers to the system's arbitrarily chosen gauge origin. The radial part is described by the exponential while the angular part is described by the spherical harmonics $Y_{l,m}(\theta,\phi)$ and a radial factor with quantum numbers l,m for spherical GTOs and described by a polynomial of cartesian coordinates for cartesian GTOs. Additional quantities used in eq. (3) and (4) include the contraction coefficients $N_{\mu j}$ and $\tilde{N}_{\mu j}$ which also contain the normalization of the entire contracted GTO as well as the fixed exponents $\alpha_{\mu j}$. The angular momentum quantum number of the spherical basis $L^\mu = a_x^\mu + a_y^\mu + a_z^\mu$ represents the type of atomic orbital (AO), with $L^\mu = 0$ for s-type orbitals, $L^\mu = 1$ for p-type orbitals, and so forth. There exist a variety of methods capable of efficiently calculating two-electron integrals over LAOs and the interested reader is

referred to the extensive literature on this subject.[10,37,43,44]

Integrals over spherical GTOs can be represented through Cartesian GTOs via a linear transformation.[54] Since the general concepts concerning approximate screening techniques discussed in this work are not dependent on whether or not these transformation coefficients are taken into account, we limit the following discussion on the screening of integrals over Cartesian GTOs.

2.1 Cauchy-Schwarz Screening

In the following, we introduce and compare different types of integral screening techniques for four-center integrals over complex LAOs. We start this discussion with the commonly employed Cauchy–Schwarz screening. In contrast to the other methods described in this work, it is rigorous and follows directly from the Cauchy–Schwarz inequality:[44]

$$|(\mu\nu|\kappa\lambda)| \leq \sqrt{|(\mu\nu|\nu\mu)|}\sqrt{|(\kappa\lambda|\lambda\kappa)|}. \tag{5}$$

An entire batch of integrals can be screened by evaluating the largest integrals contained therein. The real-valued quantity $T_P = \max(T_{\mu\nu}) = \max(\sqrt{|(\mu\nu|\nu\mu)|})$ is evaluated once at the beginning of a quantum chemical calculation and stored in memory, with $P := \mu\nu$ referring to a shell-pair. If we similarly define $Q := \kappa\lambda$ and $T_Q = \max(T_{\kappa\lambda})$, we can rewrite the Cauchy–Schwarz inequality as

$$|(\mu\nu|\kappa\lambda)| \leq T_P T_Q. \tag{6}$$

By evaluating $T_{\max} = \max(T_P)$, we can deduce that

$$|(\mu\nu|\kappa\lambda)| \leq T_P T_{\max} \tag{7}$$

and as such, no information about shell-pair Q is required for the screening if T_P is sufficiently small. Here, the Cauchy–Schwarz screening demonstrates the important properties that we require of any (approximate) screening technique.

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- **Separability**. All screening quantities must belong to either shell-pair P or Q, allowing us to screen shell-pairs independently of one another.

- **Boundedness**. All screening quantities must be bounded to prevent integral estimates from diverging. Thereby introducing tight bounds is especially crucial for maintaining screening efficiency.

Both criteria are fulfilled by eq. (6) and (7), respectively.

2.2   Overlap Screening

In order to further reduce the computational effort of quantum chemical calculations, approximate screening techniques can be applied in addition, particularly for highly contracted basis sets. There, Cauchy–Schwarz often does not screen an entire batch of (contracted) integrals, in which only a few of the primitive basis functions provide meaningful contributions.
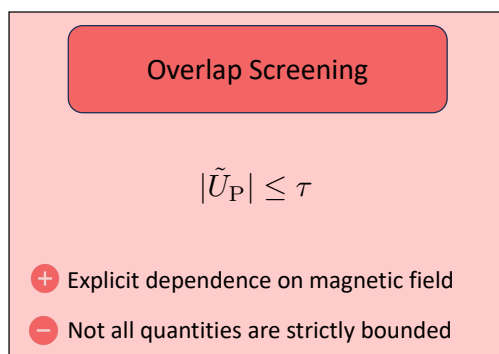

Figure 1: Overview over the approximate Overlap Screening variant.

The most commonly used types of approximate integral screening for four-center two-electron integrals rely on an evaluation of the two-center overlap integrals over s-type functions.[45–48] The idea behind such an approach is fairly simple. A two-electron integral is used to describe the interaction between the two shell-pairs P and Q. If the overlap of shell-pair P is sufficiently small, then there can be no relevant interaction between the charge density distributions of P and Q. Hence, the corresponding integral can be screened. For LAOs, the overlap between two primitive

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s-type functions is defined as[37,43]

$$\tilde{U}_{\mathrm{P}} = U_{\mathrm{P}} K_{\mathrm{P}} = \langle \mathbf{0} | \mathbf{0} \rangle \,, \tag{8}$$

where U_{P} is the overlap of two real-valued GTOs and K_{P} corresponds to a field-dependent part:

$$U_{\mathrm{P}} = N_{\mu} N_{\nu} e^{-\eta_{\mathrm{P}}(\mathbf{R}^{\nu} - \mathbf{R}^{\mu})^2} \left(\frac{\pi}{\zeta_{\mathrm{P}}} \right)^{3/2} \,; \tag{9}$$

$$K_{\mathrm{P}} = e^{-\zeta_{\mathrm{P}}(\chi_{\mathrm{P}}^2 + 2i\mathbf{P}\cdot\chi_{\mathrm{P}})} \,. \tag{10}$$

For this definition, a variety of primitive shell-pair quantities has been introduced,[37,43]

$$\zeta_{\mathrm{P}} = \alpha_{\mu} + \alpha_{\nu} \,, \tag{11}$$

$$\eta_{\mathrm{P}} = \zeta_{\mathrm{P}}^{-1} \alpha_{\mu} \alpha_{\nu} \,, \tag{12}$$

$$\mathbf{P} = \zeta_{\mathrm{P}}^{-1} (\alpha_{\mu} \mathbf{R}^{\mu} + \alpha_{\nu} \mathbf{R}^{\nu}) \,, \tag{13}$$

$$\chi_{\mathrm{P}} = (4\zeta_{\mathrm{P}})^{-1} \mathbf{B} \times (\mathbf{R}^{\nu} - \mathbf{R}^{\mu}) \,, \tag{14}$$

where we have omitted the contraction index j for the sake of brevity. Similar definitions to those in eqs. (11) – (14) can be derived for shell-pair Q. A four-center integral is proportional to the product of (complex) overlaps between two *s*-type functions,[40,41,43]

$$(\mu\nu|\kappa\lambda) \propto \tilde{U}_{\mathrm{P}} \tilde{U}_{\mathrm{Q}} \,, \tag{15}$$

which suggests that these can be used for an approximate integral screening. This idea was recently introduced in Refs. 37 and 43. In the context of this work, we refer to it as **Overlap Screening** (Fig. 1). If the absolute value of either of the *s*-type overlaps is below a certain threshold, $\left| \tilde{U}_{\mathrm{P}} \right|, \left| \tilde{U}_{\mathrm{Q}} \right| \leq \tau$, the integral is neglected.

There are several advantages connected to such an approach. For contracted basis sets in particular, individual pairs of primitive functions may be screened within a contracted shell. Furthermore, an

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explicit dependence on the external magnetic field is introduced through the dependence on K_P and K_Q, see also eq. (10). With an increasing magnetic field strength, more integrals are screened. This corresponds to the well-known pressure-like effects of strong external magnetic fields induced by the confining potential in the diamagnetic term of the Hamiltonian.[1,10,11]

However, a close examination of this approach reveals that it can lead to significant errors. In practice, we have observed problems for systems where either very strong magnetic fields were applied or which had extended molecular geometries or basis sets with diffuse functions. In order to illustrate these effects, we have constructed a model system consisting of a linear chain of six equidistant helium atoms. Due to their astrophysical relevance, helium clusters are of particular interest in the context of quantum chemical investigations in the strong magnetic field regime.[1,26,38,42] For our model system, a finite magnetic field is applied in perpendicular direction to the chain. An uncontracted augmented Dunning basis set, here denoted as unc-aug-cc-pVTZ,[55,56] was used for each helium atom. In addition, a primitive s-type basis function with a variable exponent α_μ is added for each atom. The model system is illustrated in fig. 2.
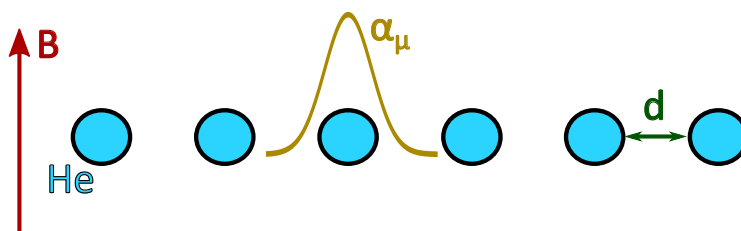

Figure 2: Model system consisting of six equidistant helium atoms in an external magnetic field **B** (red). The distance between two neighboring atoms is denoted as d (green). An additional primitive s-type function with exponent α_μ is added for each atom.

As starting conditions, we choose a magnetic field strength of $|\mathbf{B}| = 0.3\,B_0$, a distance of $d = 3\,a_0$ between neighboring atoms and an exponent of $\alpha_\mu = 0$ for the additional function. Then, we vary these three parameters individually while keeping the other two parameters fixed. The maximum error introduced for four-center integrals as well as the amount of screened integrals is depicted in fig. 3 (red curve). Please note that the other curves (blue and green) represent other approximate screening techniques introduced at a later point in this work. As a reference, the results from using

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Cauchy-Schwarz screening (orange curve) are also depicted.

As expected, the Overlap Screening introduces significant errors which become apparent with increasing magnetic field strength, bond distance and a more diffuse nature of the basis set. The error of the integral can be quite large without affecting the Hartree-Fock energy significantly. For the He$_6$ model system, we observe errors in the order of up to $1\mu E_h$. Since most of the falsely screened integrals are associated with longer interatomic distances, the corresponding density matrix elements will have a small contribution, which attenuate the error in the energy. The impact on properties however is far more significant. If we assume that the property is evaluated by numeric differentiation via finite differences with a step size of 10^{-3}, then for a first-order property the error of one µE$_h$ in the energy corresponds to an error in the third significant decimal. For a second-order property this results in an intolerable error, reinforcing the necessity of a stable screening approach. In the following we examine the reasons for this behaviour and introduce approximate screening techniques that are not plagued by these problems.

2.3 Harmonic Screening

For the Overlap Screening, it was exploited that four-center integrals are proportional to the s-type overlaps. They can be constructed as linear combinations of auxiliary integrals over s-type functions using these overlaps,[41]

$$(\mathbf{00}|\mathbf{00})^{(m)} = 2\tilde{U}_P \tilde{U}_Q \sqrt{\frac{\vartheta}{\pi}} F_m(z).$$

(16)

Here, $F_m(z)$ is the m-th order molecular Boys function.[57] We shall return to its proper definitions, as well as the definition of its argument z momentarily. First, we examine the reduced exponent of the shell-quartet

$$\vartheta = \frac{\zeta_P \zeta_Q}{\zeta_P + \zeta_Q}.$$
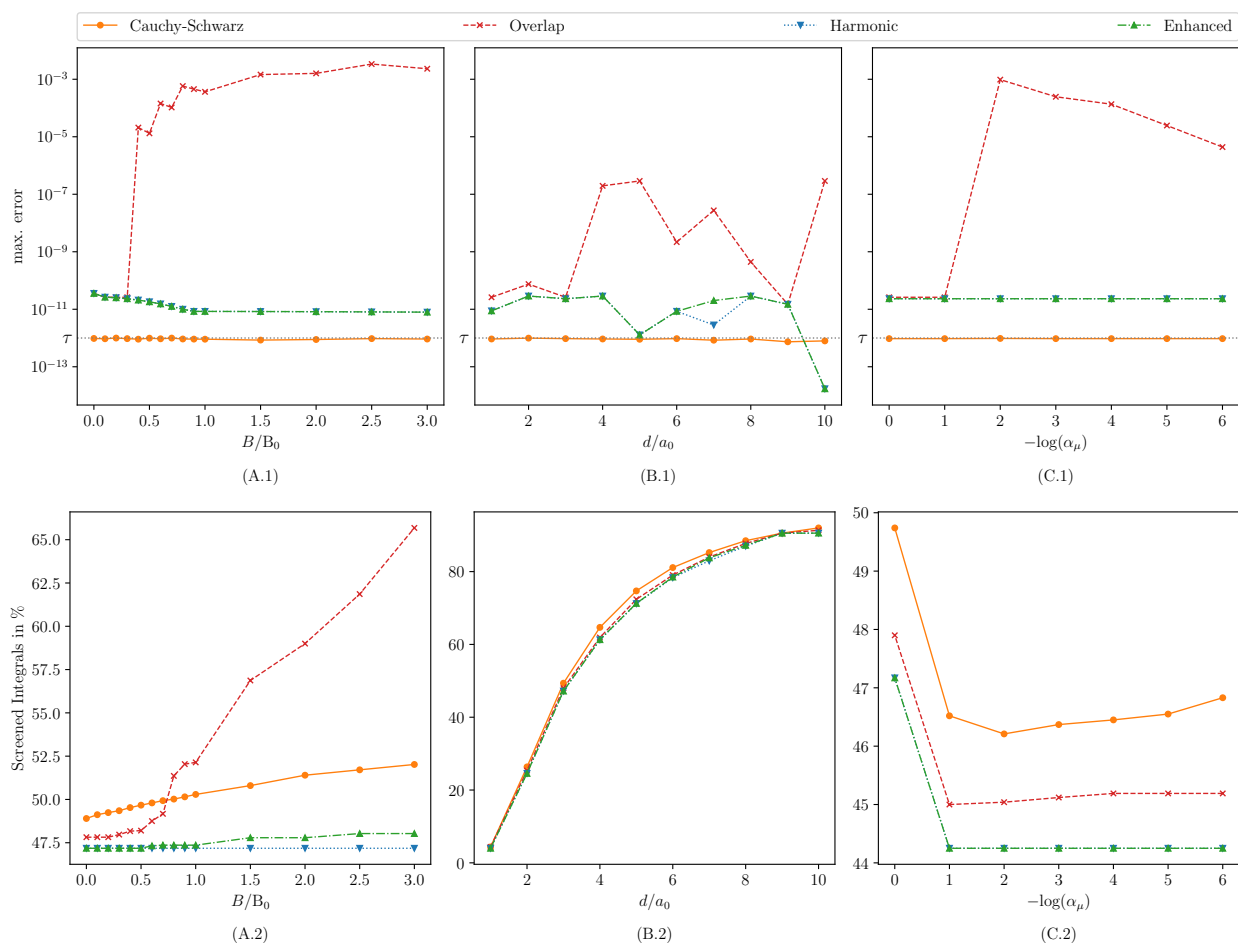
(17)

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Figure 3: Maximum error of the screened integrals and percentage of screened integrals of an equidistant He_6 linear chain in a perpendicular magnetic field. Therein, the magnetic field strength $B = |B|$, the distance between helium atoms d and the exponent α_μ of an additional s-function were individually varied. (A) He_6 at $R = 3\,a_0$ and a varying magnetic field B using the unc-aug-cc-pVTZ basis set. (B) He_6 at $B = 0.3\,B_0$ and a varying magnetic field B using the unc-aug-cc-pVTZ basis set. (C) He_6 at $R = 3\,a_0$ and $B = 0.3\,B_0$ and a varying exponent α of an addition s-function added to the unc-aug-cc-pVTZ basis set. The screening threshold was set to $\tau = 10^{-12}$.
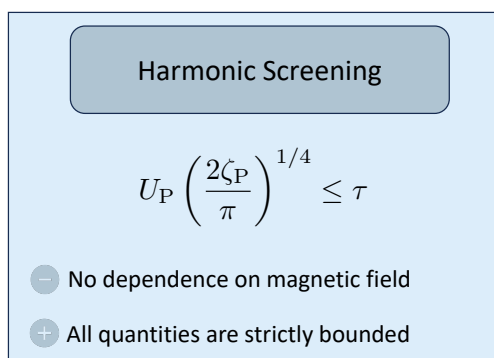
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Figure 4: Overview over the approximate Harmonic Screening variant.

We immediately notice that due to its presence, the expression in eq. (16) is generally not separable. This problem was pointed out by Häser and Ahlrichs in Ref. 45 where they present an approximate screening technique based on the harmonic mean, which is always greater or equal than the geometric mean contained in ϑ:[45,46]

$$2\sqrt{\frac{\vartheta}{\pi}} \leq \left(\frac{2\zeta_P}{\pi}\right)^{1/4}\left(\frac{2\zeta_Q}{\pi}\right)^{1/4}. \tag{18}$$

Häser and Ahlrichs used this relation to argue that the auxiliary integrals can be screened according to this relation since the molecular Boys function,

$$\begin{aligned}
F_m(z) &= \int_0^1 t^{2m} e^{-zt^2} \mathrm{d}t\,, \\
z &= \vartheta(\tilde{\mathbf{P}} - \tilde{\mathbf{Q}})^2\,, \\
\tilde{\mathbf{P}} &= \mathbf{P} - \mathrm{i}\,\chi_P\,,
\end{aligned} \tag{19}$$

is bounded for real-valued positive arguments, i.e., $|F_m(z)| \leq 1\ \forall z \in \mathbb{R}^+$. Evidently, this is always the case for real-valued GTOs. For complex-valued LAOs, however, this is no longer the case.[57] Here, the complex argument of the Boys function has a real part of

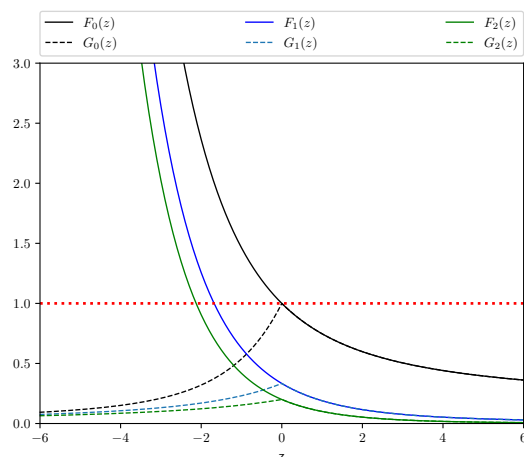$$\mathrm{Re}\,(z) = \vartheta\left((\mathbf{P} - \mathbf{Q})^2 - (\chi_P - \chi_Q)^2\right), \tag{20}$$

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Figure 5: Boys function $F_m(z)$ and auxiliary boys function $G_m(z)$ for real arguments z.

which can become negative if $(\boldsymbol{P} - \boldsymbol{Q})^2 < (\chi_P - \chi_Q)^2$. This is the case for systems with

- strong magnetic fields $\mathbf{B}$;

- extended molecules where the distance between two atoms $(\mathbf{R}^\nu - \mathbf{R}^\mu)$ becomes large;

- basis sets that contain diffuse functions, $\alpha_\mu \ll 1$.

Under these conditions, the Boys function is no longer bounded and is diverging with an increasingly negative real part of z. It should be stressed that this is the reason for the problems associated with the Overlap Screening.

In order to ensure numerical stability, Ishida[58] has argued that in these cases, the auxiliary Boys function

$$G_m(z) = \int_0^1 t^{2m} e^{-z(1-t^2)} \mathrm{d}t \qquad (21)$$

should be used in combination with the following definition of the auxiliary integral:

$$(\mathbf{00}|\mathbf{00})^{(m)} = \tilde{U}_P \tilde{U}_Q \sqrt{\frac{\vartheta}{\pi}} e^{-z} G_m(-z). \qquad (22)$$

As depicted in fig. 5, the Boys function $F_m(z)$ is strictly bounded for $\mathrm{Re}(z) \geq 0$ and the auxiliary Boys $G_m(z)$ function is strictly bounded for $\mathrm{Re}(z) < 0$.

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An approximate integral screening in the spirit of Refs. [45] and [48] can therefore be introduced for complex-valued LAOs:

$$(\mathbf{00}|\mathbf{00})^{(m)} \leq U_P K_P \left(\frac{2\zeta_P}{\pi}\right)^{1/4} U_Q K_Q \left(\frac{2\zeta_Q}{\pi}\right)^{1/4}, \qquad \mathrm{Re}(z) \geq 0, \tag{23}$$

$$(\mathbf{00}|\mathbf{00})^{(m)} \leq U_P K_P \left(\frac{2\zeta_P}{\pi}\right)^{1/4} U_Q K_Q \left(\frac{2\zeta_Q}{\pi}\right)^{1/4} e^{-z}, \qquad \mathrm{Re}(z) < 0. \tag{24}$$

However, while eq. (23) is separable, eq. (24) is not. Separability can be restored by realizing that

$$\left| K_P K_Q e^{-z} \right| \leq 1, \tag{25}$$

which enables us to combine eqs. 23 and 24 into the following inequality:

$$(\mathbf{00}|\mathbf{00})^{(m)} \leq U_P \left(\frac{2\zeta_P}{\pi}\right)^{1/4} U_Q \left(\frac{2\zeta_Q}{\pi}\right)^{1/4}. \tag{26}$$

It should be noted that this condition is not dependent on the external magnetic field in any capacity. In fact, it is equivalent to the field-free approaches that have been established for decades.[45,48] We refer to this type of screening as harmonic screening (fig. 4) due to the use of the harmonic mean for the separability criterion.

The results of this type of approximate screening on our model system are depicted in fig. 3 (blue curve). Overall, the quality of this approach is very consistent. The error is approximately one order of magnitude larger than the threshold but overall stable with respect to the varied parameters. Due to its field-independent nature, the same amount of integrals is screened regardless of the field strength (A.2). The decrease in the maximum error of an integral visible in (A.1) can be attributed to the aforementioned pressure-like effects of strong magnetic fields that are not taken into account here. It should thus be interpreted not as an increase in quality, but rather as a missed potential to screen integrals that have also become negligible due to the presence of the magnetic field.

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2.4 Enhanced Screening

While the Harmonic Screening is an overall improvement upon the Overlap Screening due to its bounded nature, it lacks the magnetic field dependency which incorporates the field-induced pressure-like effects into the screening technique. We therefore propose a new approximate screening technique that is both bounded in all quantities as well as field-dependent. This **Enhanced Screening** (fig. 6) is a straightforward extension of an idea originally proposed by Cremer and Gauss in Ref. [47], which is functionally equivalent to the approach of Häser and Ahlrichs for real-valued GTOs.[45,46] They recognized that the auxiliary integral over *s*-type functions [22] can be readily approximated using a Cauchy-Schwarz estimate. This bound is rigorous only for integrals over *s*-type functions and becomes a good approximation when considering integrals over functions of higher angular momentum.

Figure 6: Overview over the approximate Enhanced Screening variant.

For integrals over LAOs the diagonal elements of the auxiliary integrals can be approximated via

$$\text{diag}((\mathbf{00}|\mathbf{00})^{(m)}) \leq \text{diag}((\mathbf{00}|\mathbf{00})^{(0)}) = \left(U_P \left(\frac{2\zeta_P}{\pi}\right)^{1/4}\right)^2 G_0(2\zeta_P \chi_P^2). \tag{27}$$

Here, one has $\mathbf{P} = \mathbf{Q}$ and $\chi_P = -\chi_Q$. As such, the argument of the Boys function becomes $z = -2\zeta_P \chi_P^2$, while the remaining product reduces to $K_P K_Q e^{-z} = 1$. Thus, a Cauchy-Schwarz-type

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approximate screening for *s*-functions can make use of this expression to yield the estimate

$$(\mathbf{00}|\mathbf{00})^{(m)} \leq \left[U_{\mathrm{P}} \left(\frac{2\zeta_{\mathrm{P}}}{\pi} \right)^{1/4} \sqrt{G_0(2\zeta_{\mathrm{P}}\chi_{\mathrm{P}}^2)} \right] \left[U_{\mathrm{Q}} \left(\frac{2\zeta_{\mathrm{Q}}}{\pi} \right)^{1/4} \sqrt{G_0(2\zeta_{\mathrm{Q}}\chi_{\mathrm{Q}}^2)} \right] , \qquad (28)$$

which includes the magnetic field dependence in the auxiliary Boys function and converges into the Harmonic Screening in the limit of a vanishing field.

While this approach combines all of the aspects that we wanted to incorporate into an approximate screening technique for integrals over LAOs, it may not be the most practical approach. The evaluation of the auxiliary Boys function, even for real-valued arguments such as those in eq. (28) is rather expensive, and we would thus like to replace it with a more cost-efficient alternative. A better enhancement may be found by analyzing the asymptotic limit of the auxiliary Boys function:[57,58]

$$G_0(z) \approx \sum_{k=0}^{N} \frac{(2k-1)!!}{(2z)^{k+1}} \qquad , z \in \mathbb{R}^+ . \qquad (29)$$

Upon closer examination of this series, we derive the following bound:

$$G_0(z) \leq \frac{1}{z} , \qquad (30)$$

which is rigorous for all $z \in \mathbb{R}^+$. However, this bound is divergent for $z \to 0$, while the auxiliary Boys function is bounded by $0 \leq G_m(z) \leq 1$. Estimating $G_0(z)$ through the bound in eq. (30) thus only leads to an improvement for $z \geq 1$. We may combine these findings in the following bound

$$\sqrt{G_0(2\zeta_{\mathrm{P}}\chi_{\mathrm{P}}^2)} \leq \left(2\zeta_{\mathrm{P}}\chi_{\mathrm{P}}^2\right)^{-1/2} \quad ; \quad 2\zeta_{\mathrm{P}}\chi_{\mathrm{P}}^2 \geq 1 \qquad (31)$$

to approximate the Boys function for larger arguments in order to enhance the screening.

This screening approach performs well on the He_6-model system in fig. 3 (green curve). The Enhanced Screening exhibits a stable error control, comparable to the Harmonic Screening, for the varied parameters, i.e. magnetic field, distance and diffuse exponent. Note that the screening effi-

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ciency of all screening variants with respect to the interatomic distance and the exponent is quite similar. This is the case as each variant considers the real-valued overlap U_P, which decays exponentially with the distance of the nuclei. Furthermore, Cauchy-Schwarz screening is implicitly dependent on the external magnetic field, while the Enhanced Screening considers the magnetic field through the bound of the auxiliary boys function. Both approaches exhibit a visible increase of screening efficiency with the magnetic field strength. As expected, while varying the distance and the exponent the Enhanced and Harmonic screening show the same overall screening efficiency as they converge in the zero field limit.

2.5 Efficiency evaluation for contracted basis sets

Now that we have established four different screening techniques for four-center integrals over LAOs, we will discuss how well they perform on different systems depending on whether a contracted or an uncontracted basis set was used. To ensure reliable results, the anisotropy induced by the magnetic field has to be correctly covered by the basis set.[26,59] As such, calculations in strong magnetic fields predominantly employ uncontracted basis sets. In the context of this work, however, we shall consider the implications of approximate integral screening technique on both contracted and uncontracted basis sets, as future developments may introduce (anisotropic) basis sets parameterized for strong magnetic fields.[60–62]

A basis set can be distinguished by two contraction schemes, i.e., the segmented contraction scheme and the general contraction scheme.[63] In the first scheme, each primitive contributes to exactly one basis function, while the second scheme allows for a primitive to contribute to multiple basis functions of the same angular momentum. While most quantum chemical program packages can handle both variants, the underlying integral algorithms are mainly tailored to a specific contraction scheme, which in turn is reflected in their efficiency in handling the respective basis sets. In our case the integral algorithm of TURBOMOLE is based on the segmented contraction scheme, while CFOUR is based on the general contraction scheme. For the latter, one wants to

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treat all basis functions of same angular momentum in one shell to maximize the efficiency of the underlying integral algorithm, even if an uncontracted basis set is used. In this case, all arguments for contracted basis functions also hold for the grouped uncontracted basis set. To emphasize, the efficiency gain by grouping an uncontracted basis set can be seen on the model He_6 system. Here we perform a calculation using an uncontracted aug-cc-pVTZ basis with either one basis function per shell compared to a calculation where all basis functions of the same angular momentum are grouped into one shell each. The aug-cc-pVTZ (7s3p2d) basis consists of 12 primitives with functions of three different angular momenta. Thus, in the first case we have for our six atom model a total of 72 shells, while in the second case we have a total of 18 shells. With no screening at all, the grouped approach takes 58s, while the approach with one basis function per shell takes 178s; calculated using CFOUR on a Intel® Xeon® Broadwell E5-2643 v4, 3.40 GHz. This underlines the need for efficient screening variants not only for contracted basis sets but also for integral algorithms employing the general contraction scheme even when uncontracted basis sets are used.

Within the model system we have previously discussed (see figs. 2 and 3), Cauchy–Schwarz screening outperformed all approximate screening techniques with respect to both error control and screening efficiency. However, this is not generally the case for contracted basis sets. Cauchy-Schwarz screening takes into account entire shell batches of integrals, while the approximate screening techniques presented in this work are generally applied for individual contributions of primitive functions.

Let us consider an integral over four contracted LAOs, each consisting of ten primitive s-type functions. If the entire integral batch has at least one contribution that is above the screening threshold τ, it cannot be discarded. However, out of the 10^4 integrals over primitive LAOs, only a small number has a significant contribution as functions with large exponents drop off sharply and have a negligible overlap. As such, only a small fraction has to be computed.

In fig. 7, we have plotted the number of screened integrals for the He_6-model system if the aug-cc-pVTZ is used instead of its uncontracted counterpart. Due to the significant errors that potentially accompany the Overlap Screening, we are discarding this method from the discussion. While the

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overall trends are similar to those presented in fig. 3, the Harmonic and Enhanced screenings perform significantly better than Cauchy–Schwarz screening if a contracted basis set is employed.
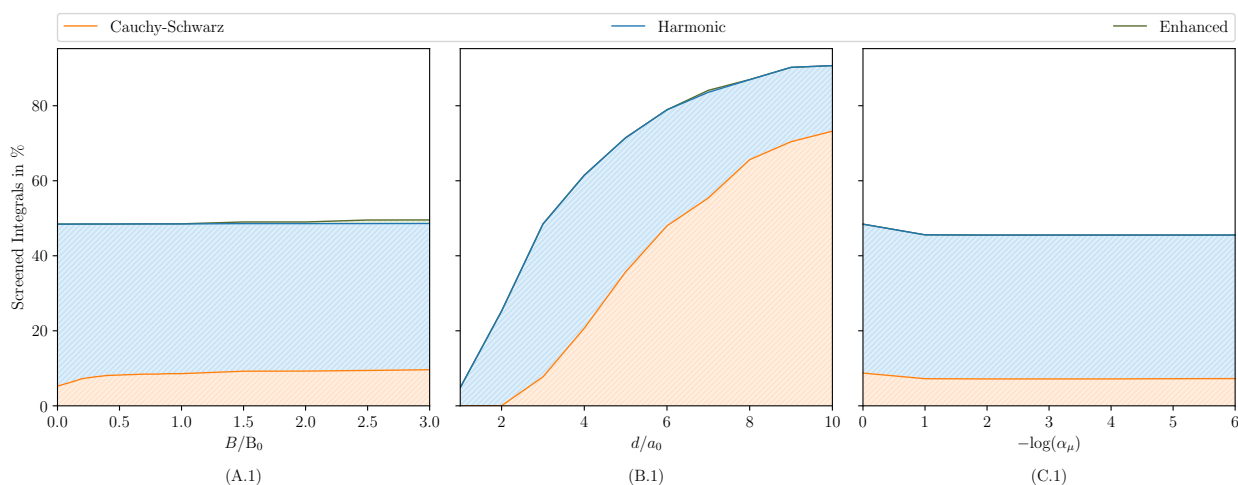

Figure 7: Percentage of screened integrals of a He_6 linear chain in a perpendicular magnetic field. Here, the system of fig. 3 was studied using a contracted basis set.

Finally, we investigate some larger systems to see how well these screening techniques perform. For this, we have performed benchmark calculations on the C_{6h}-symmetric helium clusters He_7, He_{19}, and He_{37}. The molecular structures are depicted in fig. 8, with neighboring atoms having a bond distance of 2 a_0. As the symmetry suggests,[64] we have applied the external field in a perpendicular direction to the planar clusters.

In order to compare the efficiency of the screening techniques, we have measured the computation time of one iteration of restricted Hartree-Fock (RHF) using the unc-ano-pVTZ[65] basis set. Calculations were performed on a single CPU of type Intel® Xeon® E5-2687W v4 @ 3.00GHz. Here, we used an implementation in a developer's version of TURBOMOLE based on version V7.7.1.[51–53] We compare timings for the three clusters in an external magnetic field of $B = 0.5B_0$ and $B = 2.5B_0$ (table 1), respectively. We selected the latter field strength because the perpendicular paramagnetic bonding mechanism was first described for helium in such conditions.[1] As a reference, we have performed calculations without any screening. The percentage given in parentheses is the fraction of computation time needed in comparison to a calculation in which no screening was used. As expected, all screening techniques perform progressively better if the system size is increased.
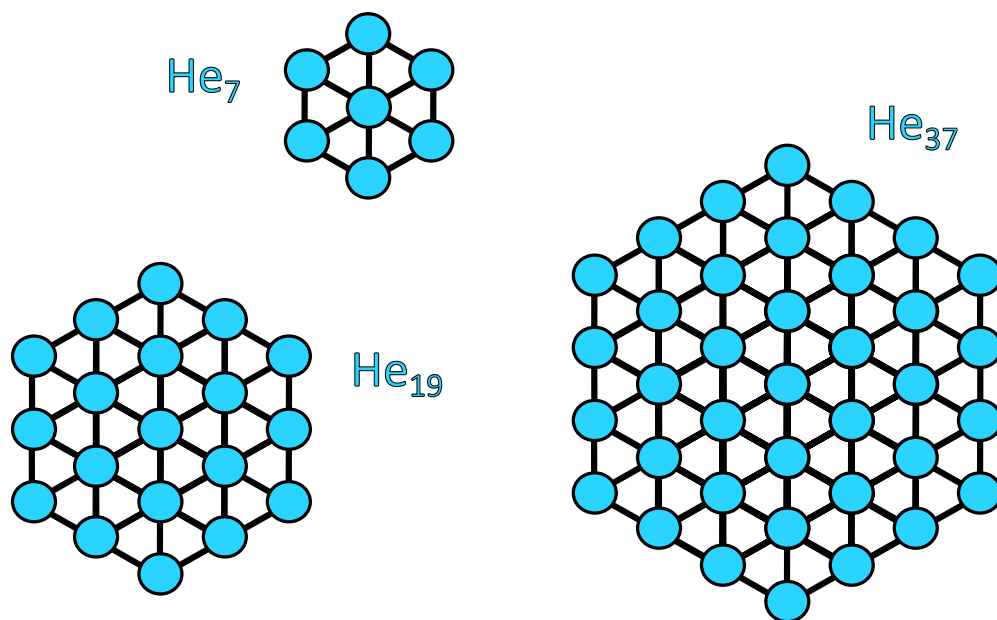
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Figure 8: Depiction of the helium clusters He_7, He_{19} and He_{37} studied in table 1 to 2.

Table 1: Wall clock timings of one restricted Hartree-Fock (RHF) iteration using an **uncontracted** ano-pVTZ basis set on the planar helium clusters He_7, He_{19} and He_{37} in a magnetic field of $0.5\,B_0$ and $2.5\,B_0$ for the introduced screening approaches. Timings relative to a calculation employing no screening are given in parentheses.

	Screening variant	He_7	He_{19}	He_{37}
B=0.5 B$_0$	No screening	24 s (100%)	1337 s (100%)	19955 s (100%)
	Cauchy-Schwarz	16 s (66.7%)	543 s (40.6%)	4837 s (24.2%)
	Harmonic Screening	20 s (83.3%)	816 s (61.0%)	8953 s (44.9%)
	Enhanced Screening	20 s (83.3%)	818 s (61.2%)	8985 s (45.0%)
B=2.5 B$_0$	No screening	62 s (100%)	4032 s (100%)	62353 s (100%)
	Cauchy-Schwarz	62 s (100%)	4026 s (99.9%)	62202 s (99.8%)
	Harmonic Screening	32 s (51.6%)	1324 s (32.8%)	13419 s (21.5%)
	Enhanced Screening	32 s (51.6%)	1324 s (32.8%)	13431 s (21.5%)

Cauchy-Schwarz screening in particular yields a significant improvement in all cases, leading to a speed-up of more than 75% for He_{37}. Overall, the approximate screening techniques perform worse than Cauchy-Schwarz screening in accordance with the results from the He_6 model system. Here, the Harmonic and Enhanced Screenings take approximately the same time, with the Enhanced Screening being slightly less efficient. This is reversed for a field strength of $B = 2.5B_0$, where the Enhanced Screening performs slightly better. In order to get further insight on how seg-

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mented contractions affect the screening, we perform benchmark calculations on the same systems, using the highly contracted ano-pVTZ basis set. The timings are given in table 2 for $B = 0.5B_0$ and $B = 2.5B_0$, respectively. Here, the approximate screening techniques outperform Cauchy-Schwarz screening by a large margin. While Cauchy-Schwarz hardly improves upon the timings of a calculation without any screening, both the Harmonic and Enhanced Screenings lead to significant speedups. For He_{37}, almost 80% of the computation time can be saved by employing either of these approximate screening techniques.

Table 2: Wall clock timings of one restricted Hartree-Fock (RHF) iteration using a **contracted** ano-pVTZ basis set on the planar helium clusters He_7, He_{19} and He_{37} in a magnetic field of $0.5\,B_0$ and $2.5\,B_0$ for the introduced screening approaches. Timings relative to a calculation employing no screening are given in parentheses.

	Screening variant	He_7	He_{19}	He_{37}
$B=0.5\,B_0$	No screening	62 s (100%)	4032 s (100%)	62353 s (100%)
	Cauchy-Schwarz	62 s (100%)	4026 s (99.9%)	62202 s (99.8%)
	Harmonic Screening	32 s (51.6%)	1324 s (32.8%)	13419 s (21.5%)
	Enhanced Screening	32 s (51.6%)	1324 s (32.8%)	13431 s (21.5%)
$B=2.5\,B_0$	No screening	62 s (100%)	4032 s (100%)	62353 s (100%)
	Cauchy-Schwarz	62 s (100%)	4026 s (99.9%)	62202 s (99.8%)
	Harmonic Screening	32 s (51.6%)	1353 s (33.3%)	13712 s (21.8%)
	Enhanced Screening	32 s (51.6%)	1351 s (33.2%)	13564 s (21.6%)

Similar to the calculations performed with the uncontracted basis sets, the Enhanced Screening only really improves upon the Harmonic Screening in a very strong magnetic field. Even then, the speedup is only about 0.2%. These findings demonstrate very clearly that for an efficient implementation of four-center integrals over LAOs, both Cauchy-Schwarz screening as well as an approximate screening technique should be used. While the former is a rigorous bound that outperforms any approximate screening technique for uncontracted basis sets (see also the discussion in Ref. 45), approximate screening techniques can lead to a significant efficiency increase for highly contracted basis sets such as the ano-pVTZ basis set used for this investigation. Combining both approaches is therefore recommended.

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3 Conclusion

Recent years have seen an ever-increasing amount of quantum chemical investigations on extended molecular structures in strong magnetic fields. For field-free calculations, efficient integral screening techniques have been used for decades in order to drastically decrease the cost associated with quantum chemical computations. In this work, we critically assessed how to adapt well-established approximate screening techniques to calculations in the strong magnetic field regime.

First, we examined the two criteria any suitable (approximate) screening technique should meet: separability and boundedness. Then, we investigated how well four different types of integral screening performed on a variety of model systems consisting of helium atoms. In addition to Cauchy–Schwarz screening, we assessed the performance of three approximate screening techniques, introduced as Overlap, Harmonic, and Enhanced screening in the context of this work. While the Overlap screening led to significant errors, especially for the determination of properties, both the Harmonic and Enhanced screenings performed well for all investigated systems. Particularly in combination with Cauchy–Schwarz screening, significant reductions in the computation time could be measured for a variety of helium clusters. For contracted basis sets or for uncontracted basis sets treated in shells within a general contraction scheme, the use of either the Harmonic or Enhanced screening are thus strongly recommended, as they combine a well-controlled error with a drastic increase in computational efficiency.

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5 Notes

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