JUnQ

Journal of Unsolved Questions

Science never fails.

Just dig through the JUnQ to find the hidden treasures!

Content

Preface

1 Mission Statement

Our vision is establishing the publication of null-results as an important cornerstone for the advancement of knowledge and scientific understanding in all disciplines thus contributing to overcome biases and fraud in research.

We want to achieve this goal by making "negative" and "null"-results from all fields of science available to the scientific community. This means that we publish scientific articles about projects where a research hypothesis is neither confirmed nor rejected, where a standard opinion in science can not be reproduced or where the desired outcome was not achieved. Most research projects produce ambiguous results, in our opinion this should be visible in publication media. The articles are peer reviewed and the decision on whether to publish a paper will be made solely by independent referees.

Furthermore, we want to foster interdisciplinary thinking by publishing short essays about open questions in science that have not been solved yet but that are of importance to the scientific community. We believe that for the advancement of science asking the right questions is more important than finding answers. The open questions are editorial board reviewed, any scientific question that does not contain false facts will be published.

Besides publishing articles and open questions, we want to create a platform for reflecting on the day-to-day business in science from a meta-perspective: Is the current scientific practice optimal for the gain of knowledge? How could we overcome prejudices that hinder objective judgement in research? What is the philosophical foundation of science? These are questions every scientist should ask himor herself, we want to provide the facilities to do so. Various formats (lectures, discussions, essays in the Journal, contributions to other journals etc.) are utilized to promote such deliberations.

The Editorial Board of the Journal of Unsolved Questions

2 Editorial Note

Dear Reader,

My first encounter with null-results in research happened right after graduating from secondary school. Not one out of a seemingly infinite number of polymerase chain reactions (PCRs) that I conducted as an intern in a molecular biology lab worked. I had tried to vary every possible parameter of the technique and at the end there was not much left to do than giving up. Frustrated as I was, I turned to a PhD student, who consoled me by showing me a list of reasons entitled "Why your PCR doesn't work". He pointed to the last item and with great disbelief I read: Bad karma, God is punishing you.[1]

Back then my mind was filled with Popper's idea that "the striving for knowledge and the search for truth are the strongest motives of scientific discovery".[2] But after this incident I began to have doubts: Is this how exact science really worked, like black box and black magic, relying on belief rather than knowledge?

Naive as I was, I did not understand that this ideal ivory tower of science is not as immaculate as I had imagined it, that the "free competition of thought" [2] is frequently biased by irrational human weaknesses, by politics, money, fashion – and last but not least current publication practices. During my scientific upbringing I stumbled upon several absurdities where – in my humble opinion – publication practices simply hindered the advancement of science. For example the organic reaction one of my supervisors had thought of. It looked great in paper-and-pencil chemistry but mysteriously did not work, no matter how hard we tried. Why was such a curious case not publishable anywhere? Or the power that an editor had over the methodology that was utilized in one of my projects – if you did not use the editor's own methodological developments he would not rate the paper as publishable.

Digging deeper into such occurences reveals that these were not only some unlucky events in the life of an undergraduate trying her first careful steps on the stage that is science. Let us look at some established facts.

In the 1990s a hot frenzy in evolutionary biology emerged after the exciting finding that females are more likely to mate with a male exhibiting mirrored halves. Set off by a Danish zoologist, who measured the symmetry of male barn swallows' feathers and correlated it with their reproductive success, scientists found the effect everywhere, in all kinds of species. Since mutations have long known to be related to the asymmetrical appearence in a being – to "fluctuating symmetry" – the results seemed extremely plausible. But then suddenly this remarkable connection between aestethics and genetics seemed to fall apart. While in the

early 1990s almost all independent studies confirmed the original finding, in 1997 only four of twelve published studies yielded positive results.[3,4] What had happened to fluctuating symmetry?

A biologist of the University of Western Australia, Leigh Simmons, gives a hint. Trying to apply fluctuating symmetry theory to horned beetles he could not confirm the effect. Bad enough, but he states that "the worst part of it was that when I submitted these null-results I had difficulties getting them published. The journals only wanted confirming data. It was too exciting an idea to disprove, at least back then".[4]

How does that fit with the free competition of thought?

Let us switch to genetics. As pointed out in the beginning, a big portion of molecular biology techniques seems somehow related to black magic rather than reproducibility and unambiguity. Various investigations show that this is not only the subjective impression of a helpless intern. When John Ioannides, professor at the University of Boston, Massachusetts, and co-workers tried to reproduce micro-array based gene expression analyses in two independent teams, they could only reproduce two out of 18 analyses published in Nature Genetics (2005-2006) fully. They state that the discrepancies were only partially due to obtaining different results, most difficulties were caused by incomplete data and by ambiguous specification of the methods.[5]

In which way does it help the advancement of knowledge if in the majority of studies important methodological information is held back making the results irreproducible?

The readers may remember the scandal involving Jan Hendrik Schön that shook the world in 2002. The German physicist working at the Bell Laboratories had knowingly falsified data for at least 3 years and – although loads of groups jumped on the train of his extraordinary findings – nobody noticed.[6]

Could this have been partially avoided by making also null-results available to the public or by requiring more raw data to be submitted in a publication?

One last example, this time from organic chemistry. Flipping through recent literature covering the art of organic synthesis, the reader will find that most conducted reactions end up having a yield of >95%. It seems impossible to publish the synthesis of a natural compound or a new method involving a reaction yield lower than this threshold. If you have ever worked in organic synthesis, you probably share the scepticism about such high yields with Tomas Hudlicky and Martina Wernerova from Brock University in St. Catherines, Canada, who sat down to assess yields in organic chemistry reported from 1955 to 2005 [7]. The study revealed that the habitual report of these almost perfect reaction yields started only in the 1980s - and to a large degree the reproducibility gets lost at this point in time as well. Carefully measuring yields during the process of extracting the pure product from the reaction mixture, the authors argue that in each work up operation around 2% of the product is lost. If an organic reaction requires the usual 3 work up steps (extraction, filtration, evaporation) yields >94% are considered unrealistic.

The reasons that the authors identify for those obviously flawed reaction yields are twofold. One is the difficulty to measure yields precisely, as the reaction scale decreases – and it steadily has decreased since the 1980s. The second is the pressure on the scientist for his method to be outstanding in the flood of published syntheses and the related tendency of the scientist to "deliberate adjustments" as the authors term it. [8]

In a recent meta-survey, Daniele Fanelli from the University of Edinburgh fixed the number of scientists who admitted to knowingly fabricate or falsify data to around 2%. [9] But in the above example a whole community knows that scientists are "deliberately adjusting" their reaction yields and everybody just plays along?

In my opinion all the examples mentioned above and the numerous ones that did not find their way into this editorial note can only lead to one conclusion: We cannot cope with bad scientific practice by simply introducing an "ethics of science" course to all undergraduate curricula. We need to start with a change in the current publication practices. We need a journal that comprehensively celebrates an alternative handling of the Big Unknown, a journal that honestly shows how many scientific projects end up with ambiguous or irreproducible data thus changing the "winning" culture of science into a "losing" culture – and a "losing" culture it definitely is, since most scientific efforts show us how little we actually know.

There are some jewels among the journals that partially fulfill these demands. In organic chemistry, *Organic Syntheses* [10] should be mentioned, a journal that has been active since 1914 and reproduces every submitted reaction procedure in one of the labs of the editors, or the *Journal of Articles in the Support of the Null Hypothesis* that publishes experimental studies from all areas of psychology that did not reach statistical significance in order to avoid bias of editors or reviewers against studies that did not reject the null-hypothesis.[11] In medical sciences, the *Journal of Negative Results in Biomedicine* should not be forgot, which also focuses on publishing excellent scientific work with negative or null results.[12]

Founding *JUnQ*, the *Journal of Unsolved Questions*, we want to tie all the loose ends of all those innovative ideas together to establish a universal and interdisciplinary platform for publishing, discussing, and reflecting on the importance of null-results and open questions in order to reintroduce the ideal of the "free competition of thought" to the publication business.[13]

A lot of students, post-docs, and professors whom we talked to in the course of the last half year told us that they did not believe any scientist would admit to "have failed" with his research project so openly. At JUnQ we believe that null-results should not be considered a "failure", but that one should make the best of them – they might be a missing piece in the puzzle of knowledge that we are trying to solve. I think the first issue of JunQ that you, dear reader, are holding in your hands is a sign that this idea might be successful. Of course, there is a lot of work left to do in order to be recognized as a reliable and sincere scientific journal. In

the next year we aim at steadily increasing the number of contributing authors and published articles in order to gain more importance and publicity within the scientific community. Our goal is a a biyearly release of JunQ, which would allow us to obtain an ISSN number within the next 36 months. Promoting JUnQ on various platforms in internet and real life, we want to persuade a growing number of scientists of the benefit of reading and publishing in JunQ. Furthermore, we are currently organizing a lecture series in the framework of the MAINZ Graduate School of Excellence entitled "Publish or Perish...?", where current topics regarding good scientific practice, ethics, and philosphy of science, and the publication business will be discussed. The first lecturer will be Prof. Dr. Siegfried Hunklinger, ombudsman of the *Deutsche Forschungsgemeinschaft* for good scientific practice, on April 13th he will talk about "Honesty in Science".

At the end of this editorial note the JUnQ editorial board would like to thank all the supporters without whom this first issue would not exist. We express our thanks to all contributing authors for being so bold to publish in this unconventional project. We thank the advisory board for ongoing support in all fields of action. Last but not least we want to thank the MAINZ Graduate School of Excellence. Within the MAINZ framework the idea for JUnQ was born and the Graduate School has strongly supported us from the start.

We wish you an enjoyable read of the first issue of JUnQ!

Leonie Mück on behalf of the editorial board

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[11] http://www.jnrbm.com/, accessed on Dec. 28th 2010
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3 What do you think about the Journal of Unsolved Questions?

JUnQ - thinking outside the box. To foster new concepts of thinking about applied projects within the framework of the Graduate School Materials Science in Mainz (MAINZ), we introduced our doctoral students to the well-known method of a think tank. JUnQ is the successful result of one of the think tank groups and shows the creativity and efforts of our doctoral students. MAINZ supports the mission of JUnQ and will introduce in 2011 the new lecture series "Publish or Perish...?" together with JUnQ. We are very happy that the first issue of JUnQ has now been published and are looking forward to a long and bright future of the journal.

Dr. Mark Bajohrs, Coordinator of the MAINZ Graduate School of Excellence, Mainz

Any scientific progress solely stems from raising questions. Thus, for the scientist generically the unsolved question is the interesting one, not the answered. Unfortunately, at present the scientific communication and publication culture leaves only little space for presenting and discussing inconclusive and ambiguous results. This constitutes a severe drawback of our research culture as it limits the possibilities for stimulating scientific exchange, being the origin of innovative ideas.

Providing a discussion platform for unsolved questions, JUnQ constitutes a unique possibility to gather the hidden treasures of scientific research. This journal truly fills a gap and contributes to turning research into a lively discussion again.

Prof. Dr. Angelika Kühnle, Johannes Gutenberg-University, Mainz

Unsolved questions are the driving force of science, so it is more than adequate that a journal focuses on them.
Prof. Dr. Jürgen Gauss, Johannes Gutenberg University, Mainz

Current research is biased by only publishing statistically significant results. Astonishingly, researchers seem often to forget that a not statistically significant result is the same as an insignificant result. Insignficant results are also in published articles oftentimes the engine for controversial discussions and radically new insights and a good counterpart for significant, but only incremental findings. Therefore I think that JUnQ may be a great forum for research that otherwise would never be shared publicly with the research community. Good luck!
Prof. Dr. Constantin Blome, European Business School, Wiesbaden

4 Questions of the Week

The Journal of Unsolved Question presents a "Question of the Week" on its homepage every week. Set up and formulated by the members of the editorial board, the main purpose of the "Question of the Week" consists in intriguing the reader by presenting topics of ongoing research. "Questions of the Week" published so far cover a wide variety of scientific fields, but share the feature to be of certain importance to several disciplines.
In the following, we present selected "Questions of the Week" from the last six months.

What is the value of the cosmological constant?
by Thomas Jagau

The cosmological constant Λ appears in Einstein's field equations that can be written as

$$R_{\mu\nu} - \frac{1}{2}Rg_{\mu\nu} + \Lambda g_{\mu\nu} = 8\pi GT_{\mu\nu}$$

where $R_{\mu\nu}$ denotes the Ricci curvature tensor, R the scalar curvature, $g_{\mu\nu}$ the metric tensor, $T_{\mu\nu}$ the energy-momentum tensor, and G the gravitational constant. The cosmological constant may be interpreted as a measure of the energy density of the vacuum and was first introduced by Einstein to ensure that the field equations allow for a stationary universe. However, when the expansion of the universe was established experimentally, Einstein abandoned the constant calling it the "biggest blunder" of his life.
Nowadays we have a rather different view of the cosmological constant. To calculate it as an energy density of the vacuum, the simplest approach consists in summing the quantum-mechanical zero-point energies of all fields known in nature. This leads to a value for Λ about 120 orders of magnitude higher than the upper limits set by cosmological observations on supernovae. Nobody knows how to make sense of this disastrous discrepancy but some physical mechanism must exist that makes the cosmological constant very small. Most likely, a fully developed theory of quantum gravity is required before the cosmological constant can be truly understood.

For a review of the physics and cosmology of the cosmological constant see:
http://relativity.livingreviews.org/Articles/lrr-2001-1/

How can altruistic behaviour arise through natural selection?
by Leonie Mück

Explaining eusociality, one of the most advanced forms of social organization in which some individuals reduce their own reproductive potential to raise the offspring of others, is one of the biggest challenges to Darwin's theory of evolution. It seems contradictory that genetically determined altruism is educed out of natural selection. Nonetheless, there is a vast number of species, e. g. ants, wasps and other insects living in colonies, but also some mole rats and other mammals - including humans - that can be characterized as eusocial.

Since the 1960s kin selection theory has dominated the reception and interpretation of eusociality. Kin selection theory is based on the concept of inclusive fitness and can be formalized by the so called Hamilton's inequality:

$$R > \frac{c}{b}$$

where R is the relatedness parameter between two individuals, c is the cost and b is the benifit. The inequality states that cooperation of these two individuals is favoured if the relatedness is greater than the cost to benefit ratio.
Recently, inclusive fitness theory has been challenged not only by empirical data but also by theoretical considerations. Nowak et al. (see reference below) show that the inclusive fitness condition is identical to the condition derived by standard evolutionary theory using mathematical modelling. Since the only criterion that is applied in inclusive fitness theory is relatedness, Hamilton's equality does not provide any additional biological insight.

Nowak et al. suggest that the full theory of eusocial evolution rather has to be described as a series of stages involving formation of groups that are tightly bound together if it becomes beneficial to them (e. g. because they have to defend themselves against enemies, predators and rival colonies). The appearance of mutations or recombination is the origin of eusocial alleles and between-colony selection favours the more advanced eusocial species. A similar scenario could have influenced the evolution of human social behaviour.

Hamilton's inequality should thus be varied to yield

$$\text{"something"} > \frac{c}{b},$$

while the components of "something" have yet to be determined. The origin of altruism still remains a mystery.
Further reading:
M. A. Nowak, C. E. Tarnita, E. O. Wilson *Nature* **466**, 1057-1062 (2010)

Is P equal to NP?
by Libor Veis

This question is one of the seven so called Millennium Prize Problems. It is in fact generally considered the most important open question in computer science.

In the following, I will very simply present the topic. **P** represents the class of decision problems that can be solved efficiently (in polynomial time) on a computer. **NP** consists of all decision problems whose solutions can be verified ef-

ficiently on a computer. And the question is whether every problem whose solution (when given) can be efficiently checked can also be efficiently solved. People believe that **P ≠ NP**, but the correct proof has not been done yet.

For further information see:
http://en.wikipedia.org/wiki/P_versus_NP_problem

What is the origin of homochirality in nature?
by Thomas Jagau and Leonie Mück

Most biomolecules can be synthesized in mirror-image shapes. Yet in organisms, amino-acids are always left-handed, and sugars are always right-handed. Typically, the alternative form of a biomolecule is inactive and sometimes even toxic to living things. The origins of this preference remain a mystery.

Several theories put forward over the past decades emphasize that chiral selectivity is a natural consequence of the evolution of enzymes toward maximum catalytic efficiency. In this framework, an early random event is said to have caused the enantiomeric imbalance. Many current studies

focus instead on the possibility that the preponderance of building blocks on earth were homochiral from the outset, their configurations set by a process of asymmetric amplification from a small initial excess of one chiral sense in a precursor pool. The discovery of an enantiomeric imbalance in the Murchison meteorite has even led to the idea of an extraterrestial origin of homochirality.

An overview of approaches to solve the mystery of homochirality is conveyed by the following series of papers:
Orig. Life Evol. Bios. **40**, 1-118 (2010).

Articles

Call for Another Seward: Optimization of F12 Integral Evaluation

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Explicitly correlated F12 theories have been developed in the past decades to rectify the slow convergence of dynamical electron correlation models with basis size, in which additional two-electron integrals over F12 kernels are required. This article reviews some existing algorithms for these integrals, including the author's attempt, and leave an open question: what will be the most efficient algorithm (and who wants to implement it into a tightly optimized code)?

1 Introduction

In 1867, William H. Seward (the 24th United States Secretary of State) purchased Alaska, the western frontier at that time, from Russia for 2 cents per acre. Back then, the purchase was mocked by the public as "Sewards's Icebox" [1]. After 150 years, however, his decision has proven right: Alaska is now known for its huge reserves of natural resources. Therefore, he has been a symbol of being bold to do what one believes is important yet is apparently useless.

In early 1990's, Lindh and coworkers have worked on electron repulsion integral (ERI) evaluation [2], which they wrote was "an exhausted scientific area with no room for innovation." They named the code SEWARD. Their effort has nonetheless turned out to be very valuable; all the users of MOLCAS and MOLPRO have benefited from his efficient integral routine, saving much time and perhaps increasing their number of publications. It is amazing that SEWARD is still among the most efficient integral routines after almost two decades.

There is yet another western frontier in theoretical chemistry: F12 integrals. Explicitly correlated R12 or F12 theories, which originate from Kutzelnigg's seminal work in 1985 [3], have been successful to ameliorate the slow convergence of the conventional electron correlation methods with respect to basis size [4, 5, 6]. They introduce the so-called correlation factor which explicitly depends on the electron–electron distance r_{ij} to properly describe electronic wave functions around the coalescence of two electrons. In early developments, a linear function [$f(r_{12}) = r_{12}$] was used for the correlation factor; in 2004, however,

Ten-no introduced a short-ranged Slater-type geminal function (STG) [$f(r_{12}) = e^{-\gamma r_{12}}$] [7], which has been shown to improve both accuracy and numerical stability over a linear function and exclusively used in the community. In F12 theories with the so-called approximation C [8], one needs to evaluate four types of two-electron integrals,

$$(pq|rs)_S \equiv \iint d\mathbf{r}_1 d\mathbf{r}_2 \phi_p(\mathbf{r}_1)\phi_q(\mathbf{r}_1)f(r_{12}) \qquad (1)$$
$$\times \phi_r(\mathbf{r}_2)\phi_s(\mathbf{r}_2),$$

$$(pq|rs)_Y \equiv \iint d\mathbf{r}_1 d\mathbf{r}_2 \phi_p(\mathbf{r}_1)\phi_q(\mathbf{r}_1)\frac{f(r_{12})}{r_{12}} \qquad (2)$$
$$\times \phi_r(\mathbf{r}_2)\phi_s(\mathbf{r}_2),$$

$$(pq|rs)_U \equiv \iint d\mathbf{r}_1 d\mathbf{r}_2 \phi_p(\mathbf{r}_1)\phi_q(\mathbf{r}_1)U_{12} \qquad (3)$$
$$\times \phi_r(\mathbf{r}_2)\phi_s(\mathbf{r}_2),$$

$$(pq|rs)_X \equiv \iint d\mathbf{r}_1 d\mathbf{r}_2 \phi_p(\mathbf{r}_1)\phi_q(\mathbf{r}_1)f(r_{12})^2 \qquad (4)$$
$$\times \phi_r(\mathbf{r}_2)\phi_s(\mathbf{r}_2),$$

where U_{12} is the double commutator of $f(r_{12})$ with the kinetic operator

$$U_{12} = \tfrac{1}{2}[f(r_{12}), [-\tfrac{1}{2}\partial_1^2 - \tfrac{1}{2}\partial_2^2, f(r_{12})]]. \qquad (5)$$

$\phi_p(\mathbf{r}_1)$ is a one-electron Cartesian Gaussian basis function centered at $\mathbf{P}_p$,

$$\phi_p(\mathbf{r}_1) = x^{l_p} y^{m_p} z^{n_p} \exp(-\zeta_p ||\mathbf{r}_1 - \mathbf{P}_p||^2). \qquad (6)$$

This article is intended to provide a (non-self-contained) overview of the existing algorithms to evaluate these inte-

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[2] This work was done when the author was at Quantum Theory Project, University of Florida.

grals and to leave a question on the best algorithm for those integrals.

2 Background

2.1 Electron repulsion integrals

Before going into the details on the F12 integrals, let us briefly review some algorithms for ERI evaluation. Since the ERIs are fundamental quantities on which all the electronic structure theories are based, a large amount of effort has been devoted for the efficient evaluation of ERIs:

$$(pq|rs) \equiv \iint d\mathbf{r}_1 d\mathbf{r}_2 \phi_p(\mathbf{r}_1)\phi_q(\mathbf{r}_1) r_{12}^{-1} \phi_r(\mathbf{r}_2)\phi_s(\mathbf{r}_2). \tag{7}$$

The key is to use the integral representation of the integral kernel proposed by Boys more than a half century ago [9]:

$$r_{12}^{-1} = \frac{2}{\pi^{1/2}} \int_0^\infty e^{-r_{12}^2 u^2} du. \tag{8}$$

After simple algebra, one obtains [10],

$$(pq|rs) = \eta \int_0^1 w_{\text{eri}}(t) I_x(t) I_y(t) I_z(t) dt, \tag{9}$$

$$w_{\text{eri}}(t) = \frac{e^{-Tt}}{2\sqrt{t}},$$

where I_x, I_y, and I_z are monic *polynomials* of t. η and T, as well as I's, are dependent on the position, exponent, angular numbers, and contraction coefficient of the Gaussian functions. A recent paper by Flocke *et al.* [11] is pedagogical to understand this transformation.

One way of evaluating ERI is to rewrite Eq. (9) as

$$(pq|rs) = \eta \sum_{m=0}^N i_m F_m(T), \tag{10}$$

$$F_m(T) = \int_0^1 t^m w_{\text{eri}}(t) dt, \tag{11}$$

where N is the sum of angular numbers of the basis functions and i_m are dependent on the parameters of the basis functions. $F_m(T)$ are basic integrals called Boys functions, which can formally be obtained by the upward recurrence relation

$$F_m(T) = \frac{1}{2T}\left[(2m-1)F_{m-1}(T) - e^{-T}\right], \tag{12}$$

$$F_0(T) = \sqrt{\frac{\pi}{4T}}\text{erf}(\sqrt{T}). \tag{13}$$

although it is very numerically unstable in practice. Therefore, interpolation or Taylor expansion using tabulated values is often used in standard packages. The Head-Gordon–Pople algorithm (HGP) [12] has introduced an efficient way to compute i_m by rearranging the original recurrence formula of Obara and Saika (OS) [13].

The other approach is to rewrite Eq. (9) as a discrete sum over Gaussian quadrature grid [14], called Rys quadrature [15, 16, 17],

$$(pq|rs) = \eta \sum_g^{\lceil N/2 \rceil} w_g I_x(t_g) I_y(t_g) I_z(t_g). \tag{14}$$

The positions t_g and weights w_g of quadrature grid are obtained formally by $F_m(T)$ with $0 \le m \le N$; owing to numerical instability, however, interpolation of tabulated data is usually used to determine the grid (see Sec. 3.1).

Among the fastest in the world is the SEWARD package by Lindh and coworkers [2]. They have introduced an efficient algorithm to build up I's in the Rys-quadrature algorithm (Hamilton and Schaefer proposed a similar algorithm independently [18]).

2.2 F12 integrals with an STG-nG

A popular approach to F12 integrals at the moment, which has been used in MOLPRO, TURBOMOLE, and MPQC, is to expand an STG to a linear combination of n Gaussian-type geminals or GTGs (STG-nG) as

$$e^{-\gamma r_{12}} = \sum_{i=1}^{N_g} c_i e^{-\alpha_i r_{12}^2}. \tag{15}$$

Usually $N_g = 6$ is used for practical applications. Among others, the one proposed by Alrichs [19] is very efficient; it is based on the fact that the Obara–Saika recurrence relation [13] (and hence HGP relation [12]) holds for any combined GTG and Coulomb integrals. The basic integrals can be explicitly written as follows [20]. For $(pq|rs)_S$, $(pq|rs)_X$, $(pq|rs)_Y$, and $(pq|rs)_U$

$$H_n^{(S)}(\rho, T) = \sum_i^{N_g} \eta_i e^{-\rho_i T}, \tag{16}$$

$$H_n^{(X)}(\rho, T) = \sum_{i=1}^{N_g} \sum_{j=1}^i (2 - \delta_{ij})\eta_{ij}\rho_{ij}^n e^{-\rho_{ij}T}, \tag{17}$$

$$H_n^{(Y)}(\rho, T) = \sum_{i=1}^{N_g} \tilde{\eta}_i e^{-\rho_i T} \sum_{m=0}^n {}_nC_m \rho_i^{n-m} \hat{\rho}_i^m F_m(\hat{\rho}_i T), \tag{18}$$

$$H_n^{(U)}(\rho, T) = \sum_{i=1}^{N_g} \sum_{j=1}^i (2 - \delta_{ij})\bar{\eta}_{ij}\rho_{ij}^{n-1} \tag{19}$$
$$\times (a_{ij} + b_{ij}T - n\hat{\rho}_{ij})e^{-\rho_{ij}T}.$$

ρ's contain all the information on the exponents of GTGs. The definition of ρ_i, ρ_{ij}, etc. is out of the scope of this article; interested readers should refer to Ref. [20]. The F12 integrals can be obtained simply by replacing $F_m(T)$ with these quantities in ERI evaluation codes, since the recurrence formula stays the same. The implementation of F12 integrals based on Alrichs' algorithm has been reported by Höfener *et al.* [20] in TURBOMOLE and recently also by Knizia as an efficient F12 integral core of MOLPRO [21].

We note in passing that there has been an attempt called HYPER-PRISM by Lambrecht and Head-Gordon [22]. Valeev has implemented a similar scheme with computer algebra and automated tuning [23].

2.3 F12 integrals with a genuine STG

The evaluation of F12 integrals using an STG has been invented by Ten-no in his ingenious work in 2004 [7]. It is based on the integral representation of the Yukawa potential,

$$\frac{e^{-\gamma r_{12}}}{r_{12}} = \frac{2}{\pi^{1/2}} \int_0^\infty e^{-u^2 r_{12}^2 - \frac{\gamma^2}{4u^2}} du, \qquad (20)$$

which can be derived by successive application of Fourier and Laplace transformation to the Yukawa potential. By a similar transformation to that for ERI, one obtains [7]

$$(pq|rs)_Y = \eta \int_0^1 t w_{\text{slater}}(t) I_x(t) I_y(t) I_z(t) dt, \qquad (21)$$

$$w_{\text{slater}}(t) = \frac{e^{-Tt+U(1-t^{-1})}}{2t\sqrt{t}}.$$

T and U are dependent on the parameters of the basis functions, and U is proportional to γ^2 at the same time. It must be emphasized that I_x is identical to that in ERI evaluation. Moreover, Ten-no showed [7] that STG integrals can be computed by taking the derivative with respect to γ as

$$(pq|rs)_S = \eta' \int_0^1 (1-t) w_{\text{slater}}(t) I_x(t) I_y(t) I_z(t) dt. \qquad (22)$$

using the relation $(pq|rs)_S = -\frac{\partial}{\partial\gamma}(pq|rs)_Y$. As in the ERI evaluation, we can rewrite Eqs. (21) and (22) as

$$(pq|rs)_Y = \eta \sum_{m=0}^N i_m G_m(T, U), \qquad (23)$$

$$(pq|rs)_S = \eta' \sum_{m=0}^N i_m [G_m(T, U) - G_{m-1}(T, U)], \quad (24)$$

where i_m is the same quantity appearing in Eq. (10) and

$$G_m(T, U) = \int_0^1 t^{m-1} w_{\text{slater}}(t) dt, \qquad (25)$$

which is often called Ten-no's function. He also gave a three-term recurrence relation to $G_m(T, U)$ [7, 24], and implemented the OS scheme based on $G_m(T, U)$.

Given these equations, it is rather straightforward to introduce the Gaussian quadrature scheme to F12 integrals on which our development was based [25]. It replaces Eqs. (21) and (22) by finite sums

$$(pq|rs)_Y = \eta \sum_{g=1}^{\lceil N+1/2 \rceil} w_g t_g I_x(t_g) I_y(t_g) I_z(t_g), \qquad (26)$$

$$(pq|rs)_S = \eta' \sum_{g=1}^{\lceil N+1/2 \rceil} w_g (1-t_g) I_x(t_g) I_y(t_g) I_z(t_g). \quad (27)$$

Again I_x is the same as in ERI evaluation. The quadrature grid can be shared between Yukawa and Slater integrals of the same exponent. Owing to the additional factor of t_g and $1 - t_g$, the rank of quadrature is larger by one for even N. We will return to this scheme in Sec. 3.

Using a genuine STG, one can easily show that [26]

$$(pq|rs)_X = (pq|rs)'_S, \qquad (28)$$

$$(pq|rs)_U = \gamma^2 (pq|rs)'_S, \qquad (29)$$

in which $'$ means that the integrals are evaluated with STG of twice the exponent 2γ, i.e., $f(r_{12}) = e^{-2\gamma r_{12}}$. As we will see later, this serves a potential advantage of using a genuine STG.

3 Our attempt using Rys-Like quadrature

In this section, the author's attempt with a genuine STG is reviewed. Inspired by Flocke's work [see Sec. 3.1] [11, 27], we sought for an algorithm to evaluate the Rys-like quadrature grid on the fly by Wheeler's algorithm (see below). We hoped that it could be the most efficient algorithm, which nonetheless has not been realized so far [Sec. 3.2].

We therefore resorted to a (less elegant) interpolation scheme based on tabulated data in Ref. [25], which is still quite efficient especially for high-angular batches [Sec. 3.3].

3.1 Wheeler's algorithm and ERI

Let us start with the general relationship between orthogonal polynomials and Gaussian quadrature [28]. Given a weight function $w(x)$ and an interval $[a, b]$ with $w(x) > 0, x \in (a, b)$, there is a set of monic orthogonal polynomials $[P_n(x)]$ so that

$$\int_a^b P_m(x) P_n(x) w(x) dx = 0 \quad (m \neq n), \qquad (30)$$

where n and m are the rank of polynomials. There are several classical ones, for example, the Hermite polynomials $w(x) = e^{-x^2}$ on $[-\infty, \infty]$ and Laguerre polynomials $w(x) = e^{-x}$ on $[0, \infty]$. It is very easy to show that any orthogonal polynomials have a three-term recurrence formula:

$$P_n(x) = (x - \alpha_{n-1}) P_{n-1}(x) - \beta_{n-1} P_{n-2}(x). \qquad (31)$$

The classical orthogonal polynomials have a closed form for α and β, while the others do not.

An n_G-point Gaussian quadrature integrates exactly the polynomials $[f(x)]$ of ranks up to $2n_G - 1$, i.e.,

$$\int_a^b f(x) w(x) dx = \sum_{g=1}^{n_G} P(x_g) w_g. \qquad (32)$$

The positions x_g and weights w_g of quadrature grid points are connected to α_n and β_n of the underlying orthogonal polynomials: Given α_n and β_n, x_g are the eigenvalues of the tridiagonal matrix $\mathbf{Z}$,

$$Z_{ij} = \begin{cases} \alpha_i & i = j, \\ \sqrt{\beta_k} & |i - j| = 1, \ k = \max(i, j), \end{cases} \tag{33}$$

and the weights are calculated using the first element of the associated eigenvectors $(x_{j,0})$ as $w_g = x_{g,0}^2$. In principle, one can obtain the quadrature grid from the moment $M_n(x) = \int_a^b x^n w(x)\mathrm{d}x$ up to $n = n_G$:

$$\{M_n(x)\} \ (0 \leq n \leq n_G) \tag{34}$$
$$\rightarrow \{\alpha_n\}, \ \{\beta_n\} \ (0 \leq n \leq n_G) \rightarrow \{w_g, x_g\}.$$

Practically, however, the first mapping from $M_n(x)$ to α_n and β_n is ill conditioned and terribly numerically unstable. The Chebyshev algorithm is usually used instead which maps $\{M_n(x)\}$ $(0 \leq n \leq 2n_G)$ to $\{\alpha_n\}$, $\{\beta_n\}$; this is much better than Eq. (34), but still unstable and unpractical in the current context.

A much more stable way to compute the α_n and β_n (and hence quadrature grid) is called Wheeler's algorithm which uses a similar set of orthogonal polynomials. Suppose there exists a *classical* set of orthogonal polynomials $\mathscr{P}_n(x)$ which obeys $\mathscr{P}_n(x) = (x - a_{n-1})\mathscr{P}_{n-1}(x) - b_{n-1}\mathscr{P}_{n-2}(x)$, which is similar to the target polynomials $P_n(x)$ (in other words, they are defined under a similar weight and integral range). We then compute the so-called modified moments $\mathscr{M}_n(x) = \int_b^a \mathscr{P}_n(x)w(x)\mathrm{d}x$, which are in turn mapped to the quadrature grid as

$$\begin{bmatrix} \{\mathscr{M}_n(x)\} \ (0 \leq n \leq 2n_G) \\ \{a_n\} \ \{b_n\} \ (0 \leq n \leq 2n_G) \end{bmatrix} \tag{35}$$
$$\rightarrow \{\alpha_n\}, \ \{\beta_n\} \ (0 \leq n \leq n_G) \rightarrow \{w_g, x_g\}.$$

In the work of Flocke [11, 27], it has been shown that, to generate modified moments for Rys quadrature grid, one can use the generalized Laguerre polynomials $L^{-1/2}(Tt)$ and shifted Jacobi polynomials $G(\frac{1}{2}, \frac{1}{2}, t)$ for large and small T, respectively. The weight and integral range of $L^{-1/2}(Tt)$ are $e^{-Tt}/2\sqrt{t}$, $t \in [0, \infty]$ which are exact for $T \rightarrow \infty$, while these of $G(\frac{1}{2}, \frac{1}{2}, t)$ are $1/2\sqrt{t}$, $t \in [0, 1]$ which are exact for $T \rightarrow 0$. Moreover, he showed that there are efficient and stable ways to compute modified moments (based on the three-term recurrence relation),

$$\mathscr{M}_n^{(L)} = \int_0^1 w_{\mathrm{eri}}(t)L_n^{-1/2}(Tt)\mathrm{d}t, \tag{36}$$

$$\mathscr{M}_n^{(J)} = \int_0^1 w_{\mathrm{eri}}(t)G_n(\tfrac{1}{2}, \tfrac{1}{2}, t)\mathrm{d}t. \tag{37}$$

This finding allows us to compute Rys quadrature grid on the fly. The resulting code, which is the integral core of ACES III, is at least as efficient as SEWARD [11].

3.2 Difficulty with F12 integrals

Inspired by the work above, the author spent some time, hoping to establish a similar scheme for F12 integrals,

which has turned out to be extremely hard (if by any chance possible) from several reasons. One is the non-trivial expression for modified moments with the weight function $w_{\mathrm{slater}}(t)$. As one can see, in the limit of $U \rightarrow 0$, the Yukawa integrals reduce to ERIs (with an additional factor t in the denominator), from which one might expect that $L^{-1/2}(Tt)$ and $G(\frac{1}{2}, \frac{1}{2}, t)$ above are also useful for a certain range of T and U. Even though it is possible to obtain (after some algebra) the four-term recurrence relation of Eq. (36) with $w_{\mathrm{eri}}(t)$ being replaced by $w_{\mathrm{slater}}(t)$, it seems not possible to derive a similar recurrence formula for Eq. (37).

Another problem is the complicated shape of the weight function, as shown in Fig. 1. Unlike in the Rys quadrature, the shape of the weight function dramatically changes with parameters T and U with a moving pole, which makes it difficult to find appropriate classical orthogonal polynomials for modified moments.

3.3 Brute-force two-dimensional interpolation

One possible (and brute-force) way of overcoming the numerical instability is to use multiple precision floating points beyond doubles. There are standard packages GMP and MPFR, and a sophisticated wrapper MPFR C++ that provides overloaded arithmetics and mathematical functions [29]. In our experience, 1024-bit floating points are sufficient to determine quadrature grid by means of the naive Chebyshev algorithm for any T and U values.

The obvious drawback of using multiple precisions is that computation using them is *terribly slow* compared to doubles (one should recall that the current CPU's are designed to perform double precisions efficiently). It is so inefficient that it cannot be used at runtime. Therefore, we decided to compute and tabulate grid weights and positions of some selected T and U in compile time, and resort to interpolation at runtime [25]. The runtime interpolation is a two-dimensional one for each set of T and U, or more precisely, two successive one-dimensional interpolations. The cost of evaluating quadrature grids with interpolation is almost negligible for high-angular batches [less than 4% of the entire costs for $(33|33)$], but it can be a noticeable overhead (and hence not optimal) for low-angular batches. See details in Ref. [25].

4 Discussions and Prospect

4.1 Comparison of STG and STG-nG algorithms

It is not clear which is better: the use of an STG or an STG-nG. Let us first consider the cost of evaluating all four types of $(00|00)$ integrals (i.e., integrals over s-type Gaussian basis functions). For $(00|00)$ integrals, we could perhaps conclude that approaches with a genuine STG are more efficient than those based on an STG-nG. With a genuine STG, one needs to evaluate two sets of $G_0(T, U)$ and $G_{-1}(T, U)$ with the same T, which involve 4 calls of $\exp(x)$, 4 calls
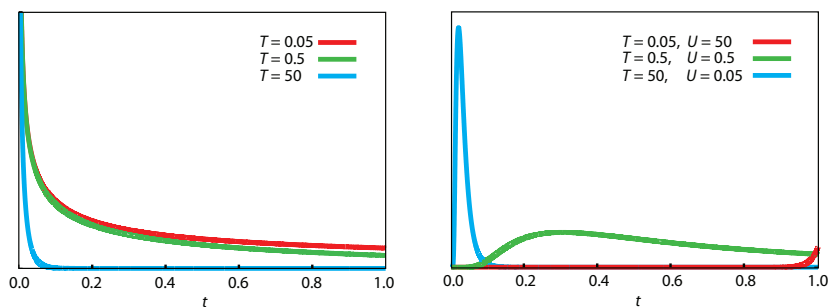
Figure 1: Weight functions for Rys and Rys-like F12 quadrature with some sets of parameters.

of erfc(x), 3 calls of $\sqrt{x}$, and some double float divisions. With an STG-6G, one needs 21 calls of $\exp(x)$ and 6 calls of erfc(x), 21 calls of $\sqrt{x}$ and some double float divisions. Next, we consider the large angular momentum limit [say, a $(44|44)$ batch]. In this case, the algorithm with an STG is again potentially more efficient. With a genuine STG, one could evaluate all four integrals with the cost three times as expensive as that of the ERI evaluation thanks to the relation $(pq|rs)_U = \gamma^2 (pq|rs)_X$ [Eqs. (28) and (29)]. This has already nearly achieved in Ref. [25]. On the other hand, the STG-6G approach is four times as expensive as the ERI evaluation.

For the intermediate angular momentum range, it is not clear which performs better, since there is no simple way to obtain $G_m(T, U)$ that contains two parameters T and U. Ten-no has implemented a code to set up $G_m(T, U)$ with various combination of algorithms, which are based on the Taylor series or continued fractions with many calls to $\exp(x)$, erfc(x), and double float divisions [24]. The Rys-like quadrature algorithm with interpolation is still applicable, but the overhead is not negligible here. The STG-6G algorithms might be competitive, or more efficient.

The fair comparison between them is further complicated since one does not need certain classes of integrals, such as $(pq|rs)_U$ and $(pq|rs)_X$ with one and two auxiliary functions, respectively. Moreover, the use of density fitting [30, 31] makes the advantage of the STG approach less pronounced for large angular quantum numbers.

4.2 An apparently useless backdoor: inhomogeneous Helmholtz equation

It is well known that the Yukawa potential is Green's function of the imaginary mass inhomogeneous Helmholtz equation (or simply, the screened Poisson equation):

$$\left(\nabla^2 - \gamma^2\right) V(\mathbf{r}) = -4\pi \rho(\mathbf{r}), \tag{38}$$

which is analogous to the Coulomb potential which is Green's function of the Poisson equation. Similar to ERI evaluations through the Poisson equation (for instance, see Ref. [32]), one can obtain $(pq|rs)_Y$ by the formula [25]

$$(pq|rs)_Y = \int V_{rs}(\mathbf{r}_1)\phi_p(\mathbf{r}_1)\phi_q(\mathbf{r}_1)d\mathbf{r}, \tag{39}$$

where $V_{rs}(\mathbf{r}_1)$ satisfies $(\nabla^2 - \gamma^2)V_{rs}(\mathbf{r}) = -4\pi\phi_r(\mathbf{r})\phi_s(\mathbf{r})$. One can also evaluate $(pq|rs)_S$ by taking a numerical derivative of $(pq|rs)_Y$ with respect to γ. We have implemented and confirmed this formula [25] using Becke's fuzzy cell grid [33, 34]. This approach is nevertheless efficient only for Coulomb integrals in pure DFT calculations where r and s are contracted by the density; the author has not been aware of any possible use in F12 calculations.

4.3 Possible Criticism

Unfortunately, one can easily formulate some criticisms to the exploration for efficient F12 integral codes. First, one could argue that the efficiency of the F12 integral evaluation is not important since the integral kernels are all short-ranged and the number of non-zero integrals is much smaller than that of ERIs. This is certainly true: for a large molecule, most of the F12 integrals can be skipped by pre-screening [35]. However, it is still important to have it efficient for small systems and perhaps even for large systems when calculated by the integral-direct mode or with the local correlation approximation.

Second criticism would be that with density fitting the most time-consuming step could be the assembly step of three center quantities, e.g., $(ia|jb) = \sum_D (ia|D)(D|jb)$, where D labels auxiliary basis functions for DF, and not the integral evaluation itself. This is again certainly true but only for large systems. Note that CC-F12 calculations are limited to relatively small systems. Furthermore, the use of local fitting domain [35] reduces the cost of the assembly step, which may legitimate the development of efficient algorithms for F12 integrals.

5 Concluding Remarks

Given the success of the F12 theories, it is now of fundamental importance to implement a tightly optimized integral routines for F12 integrals (like SEWARD for ERI). This would be much appreciated by increasing the productivity of all the people in the theoretical chemistry community.

In this article, we intentionally have not concluded which (i.e., a genuine STG or an STG-6G) should be used for the best algorithm. Although it looks to the author that the former is favorable, it is still open for discussions. In addition,

the efficiency of integral codes is determined not only by FLOP counts and the numbers of memory queries of the underlying algorithm but also by the way *how it is written* [36]. One needs to consider the cache efficiency, the numbers of function calls, loops, and condition branches, and the affinity to recent computer hardware (such as streaming SIMD extensions, general-purpose computing on graphics processing units, and so on). As pointed out by Lindh [37], it can affect the efficiency of molecular integral evaluation sometimes by an order of magnitude. In this sense, automated implementation with heuristics employed by Valeev [23] may be the way to go in a long run.

Last but not the least, we would like to emphasize that it could be an enjoyable task to realize such an optimized code; and you will be named "real programmer" [38].

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Egg-shaped Fullerene-Type and Dragon-Type Cages Unsuitable for Forming Donor-Acceptor Complexes with Noble Gases

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The discovery of the first neutral compound with chemically bound argon HArF in 2000 was a sensation in noble gas chemistry. If HArF is interpreted as a donor-acceptor complex with H^+ as an strong acceptor and F^- as a donor fragment the question arises if light noble gases helium, neon and argon could also form donor-acceptor complexes with common Lewis acids and bases like AlF_3 and NH_3. A covalent interaction between a Lewis acid, a Lewis base and a noble gas could be achieved by spatially dividing the donor and acceptor fragment thus incorporating the donor-acceptor complex into a cage-like structure. Due to the small polarizability of the light noble gases the Lewis acidity and basicity of the employed donor and acceptor must be extremely high for the noble gas to react with the cage. Novel kinds of organic donors and acceptors were designed to fullfill these criteria. These novel donors and acceptors were included in organic cages that fix geometrical conditions to be most favourable for the formation of complexes with noble gases. Among the many considered cage-types were the particularly aesthetic egg-shaped fullerene-type cages and dragon-shaped cages. Despite their beauty and their conceptual originality, they did not meet the requirements of yielding a negative reaction energy with light noble gases but they may be useful for other purposes, e. g. as hosts for hydrogen molecules.

1 Introduction

Since the first discovery of a xenon compound by Bartlett and Hoppe[1, 2] noble gas chemistry has fascinated chemists from all over the world. A broad range of reactions and compounds with xenon and krypton has been discovered since then.[3] But due to their smaller polarizability, the chemistry of the lighter noble gases is more limited. Forcing the light noble gases to be involved in chemical bonding requires extremely reactive reagents and low temperatures. Therefore the discovery of the first neutral argon compound H-Ar-F in 2000[4, 5] was a sensation. Computational analyses confirmed that in H-Ar-F argon is indeed chemically bound.[6]
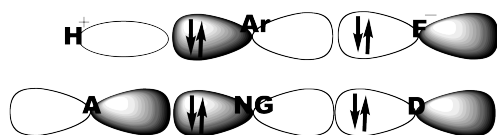

Figure 1: Bonding situation in H-Ar-F and in D-NG-A (D=Donor, A=Acceptor, NG=Noble Gas)

The bonding situation in H-Ar-F can be explained with the help of a 3-center-4-electron bond (see figure 1). The same bonding situation could be realized substituting the proton by a strong Lewis-acid and the fluorine-anion by a Lewis-base, the argon can thus be viewed to be "trapped" between an electron donating and an accepting group. However, to realize such a compound an extremely strong acceptor and donor has to be used while especially the properties of the acceptor seem to be crucial.[7]

To increase acceptor strength in organic lewis-acids, electron-withdrawing groups (e. g. fluorine atoms) can be placed close to the electron accepting atom. Electron density is then removed from the accepting atom by hyperconjugation. The acceptor strength of an ordinary Lewis-acid like AlF_3 can be enhanced by pyramidalization.[8, 9, 10, 11] Restricting F-Al-F and H-N-H angles to 109° in AlF_3 and NH_3 increases the reaction energy of AlF_3 with NH_3 enourmously compared to the reaction energy of planar AlF_3 with planar NH_3 (F-Al-F/H-N-H angles in planar molecules: 120°). In table 1 the reaction energies of pyramidalized and planar AlF_3 and NH_3 computed on different levels of theory are listed. Depending on the level of theory pyramidalization of the donor and acceptor increases the reaction energy by up to 100 $kJ\,mol^{-1}$. Recent investigations showed that there exists a minimum on the potential energy surface (PES) of F_3Al-Ar-NH_3 between Al and Ar at covalent distances, if the F-Al-F and H-N-H angles were restricted to 109.47°. No minimum between N and Ar could be detected.

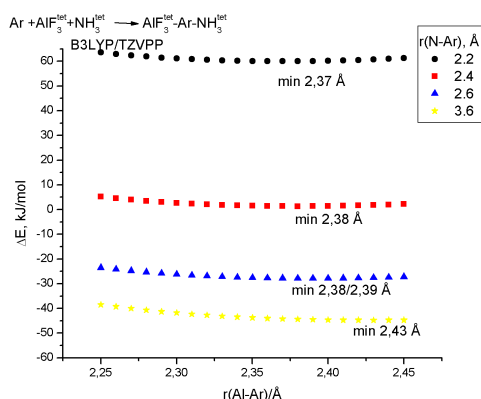[1]Johannes Gutenberg-Universität, Jakob-Welder Weg 11, 55128 Mainz, MueckL@uni-mainz.de

Figure 2: Scan of r(Ar-Al) at fixed Ar-N distances in pyra-midalized AlF_3-Ar-NH_3

In figure 2 the scan of the Al-Ar bond at several fixed N-Ar bond lengths is plotted (B3LYP/def2-TZVPP level of theory)[2]. If the Ar-N bond is sufficiently long the reaction energy is negative, which conveys favourable interaction of the donor-accpetor frame with the noble gas.[7] It should be noted, though, that optimizing the Ar-Al and Ar-N distance in AlF_3-Ar-NH_3 the complex decomposes into Ar+AlF_3+NH_3. Keeping the complex from decomposition requires connecting the donor and acceptor fragment thus keeping them at a fixed distance.

The aim of the presented project is to design donor-acceptor compounds that would entertain in chemical bonding with the light noble gases helium, neon, and argon. This is to be achieved by spatially dividing the donor and acceptor groups including them in a cage-like structure and thus fixing the geometrical conditions optimally for the noble gas to entertain in chemical bonding with the cage at covalent distances. This means that firstly the distance between donating and accepting group needs to be rigidly kept at the covalent minimum on the PES of D-NG-A (D=donor, A=acceptor, NG=noble gas). Secondly the donor/acceptor fragment should be chosen so that pyramidal geometry around the donating/accepting atom is secured. The requirements for a cage to be the host of a noble gas are therefore: 1. rigidity, 2. pyramidality of donor/acceptor fragment, 3. little repulsive interaction of the noble gas with all parts of the cage, except the donor/acceptor fragment.

Table 1: Complex formation energy of AlF_3-NH_3, ΔE (1) with pyramidalized AlF_3 and NH_3, ΔE (2) with planar AlF_3 and NH_3 , values in $kJ\,mol^{-1}$

Method/Basis Set	ΔE (1)	ΔE (2)
RHF/6-31G**	-286.6	-182.1
RHF/def2-TZVPP	-268.6	-167.7
B3LYP/6-31G**	-274.1	-180.4
B3LYP/def2-TZVPP	-254.5	-163.9
MP2(full)/def2-TZVPP	-279.8	-175.5

[2]This figure is also available in the supporting information of ref. [7]

[3]throughout the paper the following colour code of elements will be used for the figures: Carbon (grey), hydrogen (white), fluorine (yellow), aluminium (magenta), nitrogen (blue)

A plethora of cages were designed and considered, but only a fraction was successful in yielding a negative reaction energy with argon (refer to reference [7] for more details). Most did not show favourable reaction energies with the light noble gases. But although they did not meet these requirements, some of them are conceptually a lot more interesting than the cages presented in reference [7] and furthermore very aesthetic. These will be presented in this paper.

2 Computational Methods

Preliminary calculations were carried out with the Gaussian 03 program package on various levels of theory as noted.[**?**] Geometry optimization of the cages was carried out at the RHF/6-31G* level of theory using the Gaussian 03 program package. For xenon a stuttgart/RCP effective core potential was used to account for relativistic effects. In the calculations donor-acceptor complexes, the basis set superposition error (BSSE) can play an important role. The energies presented here are uncorrected for BSSE, however this error was estimated to be around 6 $kJ\,mol^{-1}$ for similar argon containing cages at the RHF/6-31G* level of theory using the counterpoise correction method as implemented in Gaussian 03.[7]

3 Egg-Shaped Fullerene-type cages

Choice of donor and acceptor For the egg-shaped cages acceptors and donors with an adamantane framework inserting Al in case of the acceptor and N in case of the donor were chosen (see figure 3)[3]. The advantage of these compounds is their rigidity. The adamantane cage does not allow geometrical rearrangement during a donor-acceptor reaction, therefore pyramidality is secured. To further increase acceptor-strength of alumoadamantane nine hydrogen atoms were substituted by fluorines. Aluminium was chosen over other group 13 elements to be the accepting center in the adamantane-type lewis acid after computing the acceptor strength of all group 13 adamantane derivatives towards NH_3 on B3LYP/def2-TZVPP level of theory. The reaction energy of the fluorinated alumoadamantane with ammonia amounts to -195.6 $kJ\,mol^{-1}$ (B3LYP/def2-TZVPP level of theory). Alumoadamantane is experimentally unknown but boroadamantane has been synthesized by Mikhailov *et al.*[12] and is stable in air and water. Boroadamantane can be utilized to synthesize N-adamantane.[13]
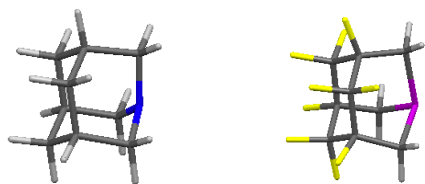
Figure 3: N-adamantane and fluorinated Al-adamantane

Cages If a suitable donor and acceptor are chosen the design of a cage comes down to building the connection between these fragments. The connection should be kept as rigid as possible to force the noble gas to a covalent distance with respect to the donor/acceptor fragment, thus in egg-shaped cages the connection between Al-adamantane and N-adamantane was chosen to contain only aromatic C_6-units resembling an egg-shaped fullerene. It is crucial to keep the diameter of the cage as large as possible in order not to bring forth repulsive interactions between the noble gas and the cage. The distance between Al and N determines which noble gas is a suitable candidate for reaction with this particular cage. All cages built in this manner are presented in figure 5 and figure 6.

Egg 1 – although perfect in form – is too large in order to obtain a covalent bond length between the noble gas and the donor/acceptor, the noble gases inserted into the other cages were chosen in correspondence to their covalent radius. Interaction energies and geometrical data are displayed in table 2. Additionally the reorganization energy E_{RO}, which corresponds to the energy needed for the geometrical changes upon insertion of the noble gas, is listed. The sum of the reaction energy and the reorganization energy should be negative for the reaction to be exothermic. Furthermore the reorganization energy can be taken as a measure for the rigidity of the cage.

The only exothermic reaction energy obtained is that of krypton being inserted into Egg 2, but looking at r(Al-Kr) and r(N-Kr) the interaction is rather of Van-der-Waals nature and not a covalent interaction. The least endothermic interaction with covalent bond lengths exhibits krypton being inserted in Egg 3 (60.1 kJ mol^{-1}), but this can hardly be called a favourable interaction between the donor-acceptor complex and the krypton. As a positive aspect should be noted that the angles NG-Al-C and NG-N-C are in all cases close to 100°, which shows that pyramidality could be ensured. The reorganization energy is mostly smaller than 10 kJ mol^{-1} which underlines the rigidity of the cage. Exceptions are Egg 2 Xe and Egg 4 Ne. The large reorganization energies can be explained by a possible repulsive interaction between the noble gas and the fullerene-type connection between the donating and accepting group. In other words, the diameter of the cages seems to be too small in order to avoid repulsive interaction with the noble gas. Due to the high number of atoms in the cages the geometry and relative energies were only calculated on RHF/6-31G* level of theory. According to table 1 relative energies on RHF/6-31G* level of theory can differ by up

to 30 kJ mol^{-1} from more sophisticated levels of theory (B3LYP/def2-TZVPP in this case). In case of a possible covalent interaction of the noble gas with the donor-acceptor fragment in this error range of 30 kJ mol^{-1} it was planned to extend the computations to higher levels of theory, but none of the egg-shaped cages came close to this range.
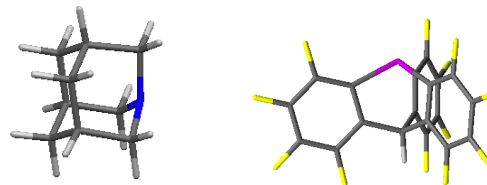

Figure 4: N-adamantane and perfluoroalumoaryl derivative

4 Dragon-type Cages

Choice of donor and acceptor For the *dragon* type cages an aluminium perfluoraryl derivative was chosen as an acceptor. Group 13 perfluoraryl acceptors of type $E(C_6F_5)_3$ (E=B,Al,Ga) are known to be extremely strong Lewis acids although the aryl groups are assembled in a planar geometry around the element E. There is still a dispute about which element – boron or aluminium – should be inserted to yield a stronger acceptor. According to Timoshkin *et al.*[14] the acceptor strength of $Al(C_6F_5)_3$ is larger than $B(C_6F_5)_3$ towards all lewis-bases except for H$^-$, therefore aluminium was used here. To enhance lewis acidity additionally the aryl groups were pyramidalized by binding them to a CH group yielding $Al(C_6F_4)_3CH$ as a sum formula (see figure 4). The reaction energy of $Al(C_6F_4)_3CH$ with ammonia is considerably lower than of alumoadamantane (244.5 kJ mol^{-1}, B3LYP/def2-TZVPP level of theory), $Al(C_6F_4)_3CH$ seems to be the stronger acceptor. Just like in the egg-shaped cages N-adamantane was used as a donor-fragment (see figure 4).

Cages To make the cage as rigid as possible, aromatic units C_6H_4 were chosen as a connection between the donor and the acceptor fragment. Differing in the number of aromatic rings within the connection, two cages with different donor-acceptor distances – dragon 1 and dragon 2 – were designed as displayed in figure 7. To further increase the acceptor strength of the $Al(C_6F_4)_3CH$ fragment, fluorine atoms were added to all positions close to the aluminium atom. It should be noted that in dragon 1 there are fluorines pointing into the cage, while in dragon 2 fluorines were only added to positions on the outside of the cage. Due to the small Al-N distance only the light noble gases were suitable candidates for reacting with both cages. In dragon 1 neon and argon were inserted while for dragon 2 only argon was tested.

The reaction energies ΔE upon inserting the different noble gases into the cages as well as the reorganization energy E_{RO} and some important geometrical data are displayed in table 3. Non of the reaction energies are neg-
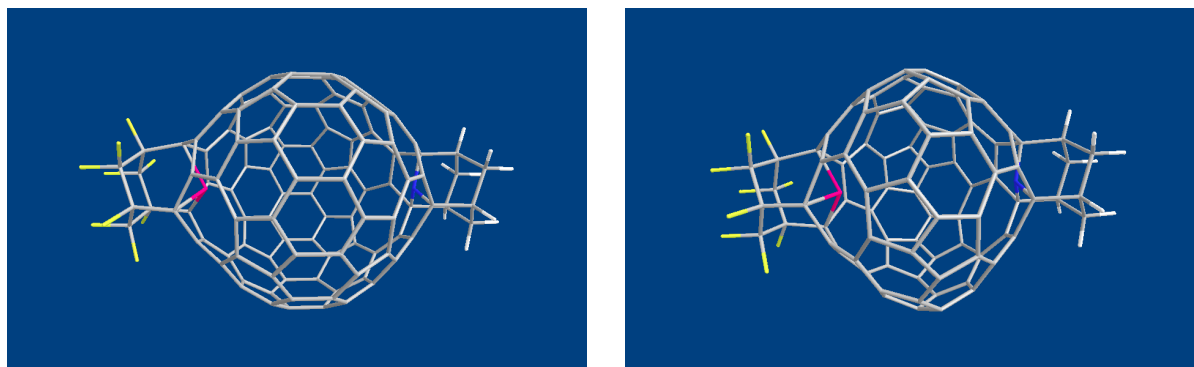
Figure 5: Left: Egg 1, r(Al-N)=8.37 Å, diameter $\approx$ 9 Å, right: Egg 2, r(Al-N)=6.38 Å, diameter $\approx$ 9 Å.
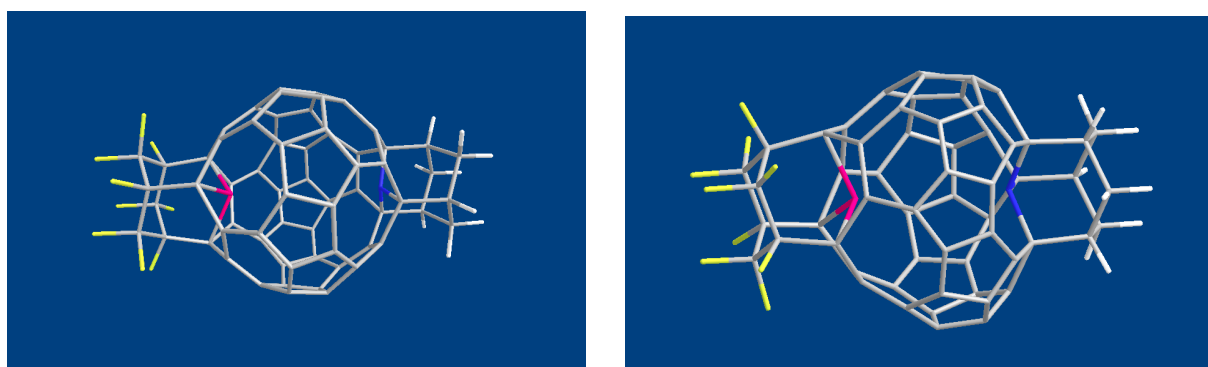
Figure 6: Left: Egg 3, r(Al-N)=5.25 Ådiameter $\approx$ 7 Å, right: Egg 4, r(Al-N)=3.88 Å, diameter $\approx$ 6.5 Å.

Table 2: Reaction energy ΔE for inserting a noble gas into an egg-shaped cage, reorganization energy E_{RO} of the cage, angles around aluminium and around nitrogen (averaged) and the distances r(NG-Al) as well as r(NG-N), RHF/6-31G* level of theory, *for Xe stutt/RCP basis set was used.

Cage with NG	ΔE, kJ mol^{-1}	E_{RO}, kJ mol^{-1}	$\angle$ NG-Al-C	$\angle$ NG-N-C	r(NG-Al), Å	r(NG-N),Å
Egg 2 Kr	-16.95	1.7	105.3 °	100.8 °	2.97	3.39
Egg 2 Xe*	71.9	39.9	105.6 °	100.9 °	2.95	3.41
Egg 3 Ar	82.8	3.3	102.0 °	102.1 °	2.49	2.85
Egg 3 Kr	60.1	7.2	102.4 °	101.9 °	2.49	2.85
Egg 4 Ne	100.0	21.5	100.0 °	106.2 °	1.92	2.27

Figure 7: Left: Dragon 1, r(Al-N)=3.76 Å, right: Dragon 2, r(Al-N)=4.65 Å.

Table 3: Reaction energy ΔE for inserting a noble gas into a Dragon type cage, reorganization energy E_{RO} of the cage, angles around aluminium and around nitrogen and r(NG-Al) as well as r(NG-N), RHF/6-31G* level of theory.

Cage with NG	ΔE, kJ mol^{-1}	E_{RO}, kJ mol^{-1}	∠ NG-Al-C	∠ NG-N-C	r(NG-Al), Å	r(NG-N), Å
Dragon 1 Ne	31.2	24.5	115.9°	107.5°	1.94	2.44
Dragon 1 Ar	118.6	54.7	115.9 °	106.7 °	2.21	2.55
Dragon 2 Ar	88.5	42.9	113.0 °	107.1 °	2.28	2.61

ative. The least repulsive interaction seems to take place between neon and dragon 1, but 31.2 kJ mol^{-1} can hardly be called favourable. Furthermore the Ne-N and Ne-Al distances are relatively large, it is questionable if a covalent bond is obtained. Reorganization energies are comparably high, the dragon-type cages are a lot less rigid than the egg-type cages.

In Dragon No. 1 the high reorganization energies (54 kJ mol^{-1} for argon and 24 kJ mol^{-1} for neon) could be explained by the fluorines in the middle of the cage being repulsed by hydrogens that are connected with the aromatic system. The angles along the aromatic units in the connection change greatly during insertion of the noble gas thus this process is high in energy. In dragon 2 the reorganization energy upon insertion of argon is lower than in dragon 1 by around 12 kJ mol^{-1}, but the absolute value (42.9 kJ mol^{-1}) is still very high. This could be explained by the fact that in dragon 2 only hydrogens – and no fluorines – point into the cage, therefore the repulsive interaction between the atoms that are "cramped" inside the cage are less pronounced.

Compared to the egg-shaped cages, the angles around aluminium are larger than in the dragon-type cages. This conveys that Al(C$_6$F$_4$)$_3$CH is less rigid than alumoadamantane, which may weaken the acceptor strength of Al(C$_6$F$_4$)$_3$CH.

5 Conclusion

In this project the bonding model of the first neutral argon compound H-Ar-F (a 4-electron 3-center bond) was applied to donor-acceptor complexes with noble gases. Since these complexes are very sensitive to geometrical changes, cages were designed to spatially divide the donor and acceptor fragment forcing the noble gas to interact with the donor and acceptor fragment at covalent distances by the rigid cage structure. Especially pyramidalization of the donor and acceptor is important as it increases the acceptor strength enourmously. Two types of acceptor fragments (alumoadamantane and Al(C$_6$F$_4$)$_3$CH) and one type of donor fragment (N-adamantane) were used to build two types of cages, namely egg-shaped and dragon-shaped ones. As a connection between the donor and acceptor fragment two types of units were utilized, fullerene-type and aromatic units. Non of the cages presented here have the desired properties of readily reacting with a light noble gas in contrast to the cage presented in Reference [7]. This is probably due to the repulsive interaction between the noble gas and the connection between the donor and the acceptor fragment that constitutes the cage-like structure. The "successful" cage of reference [7] employs a linear alkyne-

connection thus minimizing the repulsive energy between the noble gas and the cage. Another reason for the failure of the presented egg-type and dragon-type cages might an unsuitable distance between the donor and the acceptor fragment. Further investigations would be necessary to thoroughly study the reasons for the unfavourable reaction energies of the egg-type and dragon-type cage

Although the cages turned out to be unsuitable for their original purpose, they are conceptually very interesting in terms of the design of the connection between donor/acceptor fragment and in terms of choice and construction of donor/acceptor fragment. Possibly they could be used for other purposes, e. g. trapping different atoms/molecules like hydrogen in the cages.

6 Acknowledgements

Supplementary information available Cartesian coordinates of selected cages with and without noble gases are available as supplementary material.

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Open Questions

Why Do Male Infants Have More Flatulence Than Female Infants ?

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1 Introduction

The time spent with their baby is usually the best time for parents. However, during the first three months after the baby has been born repeated screaming of the infant is observed that can be very exhausting for parents. The reason for this screaming is often a colic. The definition of a colic is *a healthy baby with periods of intense, unexplained fussing/crying lasting more than 3 hours a day, more than 3 days a week for more than 3 weeks* described by Wessel.[1] However, nowadays, the definition of a colic, called "non-Wessel's" colic, is rather considered when babies start with sudden, severe, unexplained crying lasting less than three hours per day.[2] It is interesting to note that after three to four months, this frequent appearance of infant colics usually vanishes. For a detailed overview of infant colic see for example Ref. [3].

It is discussed that colics arise due to flatulence. Many possible reasons for flatulence in the baby's digestive system have been presented and numerous suggestions how to avoid them can be found. However, there is one point that is often mentioned but, to the best of my knowledge, has never been investigated in detail so far. It is said that the number of male newborns suffering from flatulence is considerably higher than it is the case for female infants. The aim of this work is to raise the above question and to call attention of researchers in the field to this topic to help millions of parents in the world to better understand their newborns.

This paper is structured as follows. In the second section reasons for flatulence are briefly discussed. Section three deals with possible strategies to avoid flatulence. The conclusion finally summarizes the aforementioned in the context of the open question raised in this work.

2 Reasons for Flatulence

Flatulence usually occur during the first three months after the baby has been born. The reason for colics are widely discussed in the literature[3, 4] and are still unclear. When babies are born they have a very immature gut. For the first thirteen weeks of life the newborn digestive system just learns how to function. Muscles that support digestion do not work properly for moving food efficiently thought the digestive tract. Due to this food may move slower than usual through the digestive system leading to an increased formation of digestive gas. The reason for flatulence may also be that newborns do not have developed the bacterial flora that aid to digest. It is also discussed that colics are related to the fact that babies swallow air. This may happen when they are fed using bottles or when newborns start to cry and due to this swallow air. Recently, an extensive study by Shenassa and Brown indicated that a correlation of consuming nicotine by the mother and the occurrence of colics may exist.[5] Although many reasons for flatulence are discussed in the field it is not clear why these lead to a higher rate of flatulence for male infants.

3 Practical Strategies to Avoid Flatulence

As flatulence are extremely painful for babies and in this way exhausting for parents, practical strategies to avoid them are summarized here. However, the list presented here is not considered complete and many other useful ideas may have been developed over the last centuries. Furthermore, only non-medicinal and noninvasive treatments are discussed in this work.

If the baby is fed using a baby bottle, parents should pay attention that the infant does not drink too fast. Otherwise, the baby swallows much air. In this context it is important to realize that only teats are used having a suitable hole size corresponding to the infant's age. An alternative here may be to breastfeed the baby as long as possible. After feeding, babies should have the chance burp to reduce the amount of air in the stomach.

For the case that flatulence cannot be avoided it is recommended to massage the infant's belly clockwise to make the baby feel comfortable. Furthermore, the flying position,

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i.e., the baby lies on the belly on the forearm, as well as feeding fennel-anise-caraway-tea are discussed to help to reduce the pain. Especially the "5 S's" approach is worth to be mentioned at this point as it more or less summarizes all the techniques that parents can use to calm their babies, namely swaddling, side or stomach (laying the baby on the side or on the stomach), "Shhh" sound, swinging and sucking.[3]

4 Conclusion

In this paper the question has been raised why male infants suffer from flatulence more often than female newborns. Although the discussion above points out reasons for colics in general it is not clear why the statement exists that especially male babies are more prone for flatulence and how they differ in this context from their female counterparts. Further studies need to be carried out to confirm that male infants indeed have a higher rate of flatulence and to identify the reason for this. The author will continue his research in the front line. Beginning in October, investigations will be intensified to get new insight. The author also appreciates further discussions and hints that can help to unravel this open question.

5 Acknowledgments

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Is Chess Solvable?

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1 Introduction

Chess is a fun game to play, but for some people it is more than just a game. Professional chess players make a living of it. Big companies, like IBM, develop supercomputers to beat human players at chess. For hundreds of years, people have been fascinated by the game. The rules are simple and easy to learn, but achieving a high level of playing skill takes years of training and experience.

To be successful at chess, it is important to find good moves. During a game, the players are trying to successively find the best move in every position. But is there such a thing as the "best" move? Maybe there are some equally good moves. The German chess master Emanual Lasker even argued that there are as many best moves as there are different opponents. This inevitably leads to the question whether chess is solvable.

A game is called solvable if it is possible to determine the outcome before even playing. For instance, Tic-Tac-Toe is a solved game. If both sides make only perfect moves, the game will always end in a draw. In this easy case it is even possible to draw a tree for all possible moves. For every position, the end of the tree shows the possible outcomes for the possible moves. The players just need to choose the moves leading to desirable outcomes.

Chess is a full information game. The players know the position of all the pieces and, in principle, can calculate all possible outcomes. From this point of view, chess is solvable. But in contrast to Tic-Tac-Toe, the tree that describes chess has to be huge. There is extensive literature about chess opening, dealing with just the first few moves of the game. This paper raises the question, whether it is practically possible to solve chess.

2 Discussion

In a chess game, White always begins. Black can only react to the threats that White poses. For this reason, if chess can be solved, the only possible outcomes are "White wins" and "Draw". The only scenarios where having to move is bad are Zugzwang scenarios. They occur only in endgames and we assume that the effect is neglegible. The most rigorous way to solve chess would be to draw a tree for all possible positions. Then, starting from any position, a player would be able to make only perfect moves by following the branches and looking at the end of the tree for the outcome of each choice.

There are 12 distinct pieces in a chess game: King, Queen, Rook, Bishop, Knight and Pawn, each in black and white. On a chess board with 64 squares, there are $64!/52! \approx 1.57 \cdot 10^{21}$ possibilities to place those pieces. This is not tak-

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ing into account illegal and symmetric positions, but there are many more positions with more pieces, less pieces and different piece combinations. The total number of possible positions is estimated to be $\approx 2.28 \cdot 10^{46}$[1]. This number is so high that it is practically impossible to write down all the positions.

One step into the direction of "drawing trees" are the Table-bases[2]. This is a collection of endgame positions, all possible moves for these and the outcome. Up to now, all positions with 6 pieces or less have been solved, and the number is growing. Some pieces more might be feasible, but Table-bases will never include all 32 pieces of a chess game.

Most of the possible positions will look like complete rubbish to an experienced player. And for most positions, it will be obvious who wins, because of one player having an undeniable advantage. It might be enough to collect all important positions, even though this number will still be huge.

Right now, the only way to coming closer to solving chess seems to be a combination of raw computer power and clever algorithms and heuristics. Chess engines are already able to beat the best human players of the world. With faster computers it is possible to increase the search depth, the number of successive moves the programme calculates in advance. Nowadays, typical search depths are 15 and more halfmoves, far more than the average human player is able to handle. Maybe quantum computing will significantly in-crease the search depth further one day.

The weak spot of chess engines is positional evaluation, but with better algorithms and heuristics the evaluations are becoming more accurate. Additionally, there is still a lot of unexplored potential in the direction of intelligent, self-learning engines.

Combining computer power and heuristics with extensive tablebases leads to engines that are able to "solve" simple positions. The definition of simple in this context has changed dramatically in the past, and will change in the future. The solution to more complex positions, positions that are closer to the starting position, will become available.

3 Conclusion

Even though solving chess for every possible position is not possible, it might be possible to develop a chess engine that reliably finds the route to victory (or a draw) through a combination of computational power and heuristics. Whether this will be realised for the starting position some day is an open question.

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Is it True that Flatulence Is More Common in Male Infants?

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1 Introduction

Eric Prochnow raised the question why male infants suffer more from flatulence than female infants. This article implicated the following hypotheses, which are equivalent to the public opinion on excessive crying in infants: 1. There is an organic cause (flatulence) for excessive crying. 2. Flatulence is more common in male infants. The careful lecture of the article raised some more questions. The first question is, whether male infants suffer really more often from flatulence than females. The second question is, whether there is a link between flatulence or any other gastointestinal pathology and excessive crying (Wessel's colic). The reasons for flatulence in infants remain also unclear; aerophagia, proteins and drinking habits have been discussed. In my opinion, answers to these questions may be helpful to solve the question why male infants suffer more from flatulence.

2 The Question of Gender

A short research on the internet provided some insight in the public opinion on Wessel's colic. In fact, a lot of people think, that excessive crying is more common in male infants. Even some websites of insurance companies and the pharmaceutical industry (see junq.info, comments on the article "Why do male infants have more flatulance than female infants?", JUnQ,1, Issue 1-OQ, 1, 2010) state, that excessive crying is more common in male infants. A short review of current studies published on Pubmed revealed, that there is not much evidence regarding this topic. (Ta-lachian et al. 2008), (Lucassen et al. 2001) statet that male gender is not a risk factor for excessive crying. One dutch study found out, that Wessel's colic is more frequent in male infants (van der Wal et al. 1998). In general, it remains un-clear, whether excessive crying is more common in male infants, since some studies indicate that this is true, while

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others could not find any correlation between gender and excessive crying. Since these studies have been conducted in different places it also remains unclear, whether excessive crying, and the perception of excessive crying by the parents is influenced by genetic or cultural factors. This may be due to the fact that most studies were not designed in order to solve this question. Further research is neccessary to find out the truth. The results may be valuable for research projects regarding gender related differences in pain perception and communication.

3 Flatulence and Colic

The link between excessive crying and gastrointestinal pathology, e.g. flatulence is not clear. Current research indicates that there are organic causes in only 5% of the cases of excessive crying and radiographic studies did not reveal any gastrointestinal pathology- e.g. increased gastrointestinal air. (Roberts et al. 2004, Barr 1998) Still, there seems to be evidence, that excessive crying is associated with increased levels of motilin (Sehnassa et al. 2004). Since breastfeeding is the main protective factor, it seems to be possible that the baby's crying is caused either by proteins in artificial milk porducts or by the leak of any protective factor included in the mother's milk (Saavedra et al. 2003). Some research has been conducted to find out, whether parental factors influence a child's crying patterns, or whether psychological factors influence the parents' perception of the child's behaviour. But most studies regarding these topics, e.g. to find out whether anxious parents complain more often about excessibe crying, did not lead to unambigous results. One article on an iranian study stated, that birth order is a risk factor, since the first born infant would suffer from excessive crying more often.

4 Conclusion

The question, whether there is one organic cause for most of the cases of excessive crying in infants remains unsolved.

The question, whether male infants suffer more often from excessive crying remains unsolved, too. Since excessive crying is a very common problem and many myths regarding this topic are popular, further research is necessary to help parents and infants. Since there is so little real knowledge on excessive infant crying, valuable and helpful information is not easily accessible for parents. Further research e.g. using telephone interviews would not be very expensive and may provide valuable new information.

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What Is the Best Multireference Coupled-Cluster Method?

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1 Introduction

Among the most interesting problems in state-of-the-art theoretical chemistry ranks the question: How can electronic states with multireference character be efficiently treated with chemical accuracy? Multireference problems include bond-breaking processes, biradicalic species, as well as many transition-metal compounds. Their thorough understanding is of great interest for different branches of chemistry and related applied sciences. At the theoretical level, all multireference problems share the common feature of quasi-degenerate states so that strong static elec-

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tron correlation is present. A single Slater determinant built from orbitals obtained within Hartree-Fock (HF) theory [1] is therefore not a valid zeroth-order *ansatz* for the electronic wavefunction and a linear combination of several determinants, whose occupation vector differs in some active orbitals, has to be used instead to obtain a qualitatively correct description resulting in the MCSCF (multiconfigurational self-consistent field) wavefunction.[2] Unfortunately, the inclusion of dynamical electron correlation into the wavefunction is required as well in most cases to obtain chemically accurate results.

For systems qualitatively described by HF theory, single-reference coupled-cluster (SRCC) theory [3] has proven to be a powerful approach for the inclusion of dynamical electron correlation. But since the generalization of SRCC theory to the multireference case is neither obvious nor unique, a variety of multireference coupled-cluster (MRCC) *ansätze* is possible and has been proposed.[4-10] Even though considerable effort has been devoted to this field during the last thirty years, none of the available MRCC *ansätze* has evolved yet into a computational tool as successful and widely applicable as the SRCC *ansatz*.

In the following, we will give an overview of the problems that appear when the SRCC *ansatz* is generalized to the multireference case and discuss different MRCC methods that have been developed.

2 Discussion

SRCC theory is nowadays a powerful computational tool to explore energetics as well as molecular properties in a routine manner. Its main advantage over configuration-interaction (CI) methods consists in the fact that energies obtained by SRCC theory are rigorously size-extensive, which means that the correlation energy scales linearly with the system size in the limit of a large system.[11] In contrast to CI methods that use a linear wavefunction expansion, the coupled-cluster approach employs an exponential expansion of the wavefunction

$$|\Psi\rangle = e^{\hat{T}}|\Phi\rangle \qquad (1)$$

with the cluster operator defined as $\hat{T} = \sum_q t_q \hat{\tau}_q$ and t_q and $\hat{\tau}_q$ denoting cluster amplitudes and excitation operators, respectively. $|\Phi\rangle$ is a single-determinant reference state, often the HF wavefunction. The exponential *ansatz* guarantees size-extensivity of the method regardless of a truncation of the cluster operator to a certain excitation level, which is the reason for the great success of approximated schemes like CC singles and doubles (CCSD) or CC singles, doubles and triples (CCSDT).

To treat quasi-degenerate states, several approaches that introduce only slight modifications into the SRCC *ansatz* have been proposed. Among these rank for example the active space CC method [12] and the reduced MRCC method [13] that include several higher excitations into the cluster operator. Another reasonable access to the treatment of quasi-degenerate states is provided by approximately size-

extensive MRCI-based methods like the multireference averaged quadratic coupled-cluster (MR-AQCC) method [14] and the multireference averaged coupled-pair functional (MR-ACPF) method.[15] In particular, the latter methods have shown to provide reasonably accurate descriptions for several multireference cases. However, in this paper, we will focus on genuine MRCC approaches based on a multi-determinantial zeroth-order wavefunction.

Before we discuss the existing ansätze let us summarize in brief some general features that a convincing MRCC *ansatz* should fulfill from the theoretical perspective. To begin with, the *ansatz* ought to lead to a wavefunction that represents a valid parametrization of the full CI wavefunction if no truncations are applied. The *ansatz* is furthermore expected to conserve the appealing properties of the SRCC *ansatz* (1). This includes the possibility to apply truncations to the cluster operator without losing size-extensivity. From the technical point of view, a potentially successful MRCC method should be implementable as an algorithm as robust and stable as it is possible for SRCC. The computational cost should not exceed those of comparable MRCI-based methods to secure competitiveness. Since a large number of determinants is often required for a valid zeroth-order description, a factorial scaling of the computational cost with the number of active orbitals is prohibitive.

$$|\Psi\rangle = e^{\hat{T}}\{e^{\hat{S}}\}|\Phi\rangle$$
Valence-universal (VU) MRCC

$$|\Psi\rangle = \sum_{\mu=1}^d c_\mu e^{\hat{T}_\mu}|\Phi_\mu\rangle$$
State-universal (SU) and state-specific (SS) MRCC

$$|\Psi\rangle = e^{\hat{T}}|\Phi\rangle$$
Single-reference CC

$$|\Psi^\alpha\rangle = e^{\hat{T}}\sum_{\mu=1}^d c_\mu^\alpha|\Phi_\mu\rangle$$
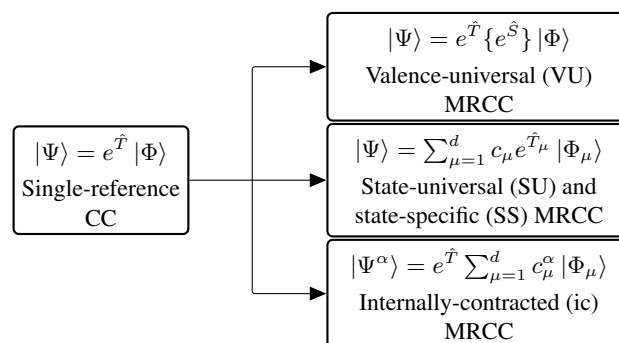Internally-contracted (ic) MRCC

Figure 1: Wavefunction *ansätze* in MRCC theory

From a high-altitude perspective all available MRCC methods can be divided into three classes, whose generic ansätze for the wavefunction are shown in Figure 1. Early attempts to formulate a general MRCC approach led to two different branches of multiroot methods that treat more than one electronic state within the same calculation. Valence-universal (VU) MRCC methods,[4] also called Fock-space CC methods, simultaneously calculate several states having different numbers of valence electrons and are closely related to the equation-of-motion (EOM) CC methods.[16] Different sectors of the Fock-space are reached via the action of the operator $\{e^{\hat{S}}\}$ on a closed-shell reference $|\Phi\rangle$.

In contrast, state-universal (SU) MRCC methods [5] cover a manifold of electronic states with a constant number of valence electrons within the same calculation. The SU *ansatz* for the wavefunction, originally introduced by Jeziorski and Monkhorst (JM), employs a linear combination of determinants $|\Phi_\mu\rangle$ as reference that form the model space $\mathcal{M}$. $\hat{T}_\mu$ and c_μ represent the reference-specific cluster operators and weighting coefficients, respectively. In SU MRCC theory the energies for all considered states and the corresponding

	VU-MRCC	SU-MRCC	BW-MRCC	Mk-MRCC	MR-expT	icSS-MRCC
intruder state free	yes	yes	no	no	no	no
size-extensivity	yes	yes	no	yes	no	yes
orbital invariance	??	no	no	no	no	yes
proper residual	yes	yes	no	no	yes	??
easy to implement	yes	yes	yes	yes	no	no

Figure 2: Comparison of several MRCC *ansätze*

weighting coefficients c_μ are obtained by diagonalizing an effective Hamiltonian matrix constructed by projecting the Schrödinger equation onto the model space

$$\sum_\mu \langle \Phi_\nu | \hat{H} e^{\hat{T}_\mu} | \Phi_\mu \rangle c_\mu = E c_\nu \ . \qquad (2)$$

The amplitude equations are defined via projection onto the set of excited determinants. The JM *ansatz* has also been employed to formulate state-specific (SS) MRCC theories that always treat only one state α within a calculation. In this case, additional sufficiency conditions have to be invoked to uniquely define the amplitudes as the JM *ansatz* leads to an underdetermined SS MRCC wavefunction. This problem relates to the fact that a certain excited determinant may be reached from more than one reference. Proposed SS MRCC approaches include the Brillouin-Wigner (BW) MRCC *ansatz*,[6] the Mk-MRCC *ansatz* [7] introduced by Mukherjee et al. and the MRexpT *ansatz* by Hanrath.[8] Equation (2) is also valid for SS MRCC approaches with the restriction that only one root of the effective Hamiltonian is physically meaningful.

Yet another MRCC approach is given by internally-contracted (ic) methods.[9,10] The ic-MRCC wavefunction is based on a reference-independent cluster operator that acts on a zeroth-order MCSCF wavefunction. Equations for determining the energy and cluster amplitudes are obtained similarly to equation (2) by projection of the Schrödinger equation on the reference space and its complement but possess a significantly more complicated structure compared to this case. While state-universal and state-specific formulations of ic-MRCC theory are principally possible, we will only discuss the state-specific variant.

After having presented some important MRCC ansätze the naturally arising question is how these ansätze perform and which advantages and disadvantages they carry. Figure 2 summarizes a couple of relevant criteria. Regarding VU and SU MRCC approaches it turns out that they carry two problems that severely limit their applicabilty, although the SU *ansatz* looks like a rather simple generalization of the SRCC *ansatz*. The first problem is obvious: In many cases, one is interested in a single root and the necessity to calculate more than one root is just a drawback that increases the computational cost. The other problem is more subtle and consists in so-called intruder states [17] that are not included in $\mathcal{M}$, but come energetically close to it at some regions of the potential energy surface. As intruder states often spoil the iterative solution of the CC equations by causing divergence problems, the choice of the model space

plays a crucial role in SU MRCC calculations.

These deficiencies may serve as a strong motivation to pursue SS MRCC approaches, which avoid the intrinsic disadvantages of SU and VU methods by always treating one single state α at a time. For SS MRCC methods based on the JM *ansatz*, the already mentioned need to introduce sufficiency conditions causes further complications. The conceptually most simple scheme is probably the Brillouin-Wigner (BW) MRCC *ansatz*, where independent amplitude equations coupled only via the effective Hamiltonian matrix are obtained for each reference. However, this *ansatz* does not preserve size-extensivity, thereby losing the main advantage of CC theory. The SS MRCC *ansatz* introduced by Mukherjee et. al. (Mk-MRCC) in contrast employs more sophisticated sufficiency conditions, which lead to explicit coupling between the amplitudes for different references and ensure rigorous size-extensivity. While the Mk-MRCC method has proven to deliver reasonably accurate results for some model applications,[18,19] it still suffers from severe limitations. One drawback, introduced via the sufficiency conditions, consists in the fact that the projected Schrödinger equation is fulfilled only in the intersection of the references' excitation manifolds but not in their union. This has been termed a violation of the "proper residual condition" [20] and motivates the MRexpT *ansatz*, which circumvents this problem by fixing the number of excited determinants to that of cluster amplitudes and thus solving the redundancy problem. While MRexpT has been shown to fulfill the proper residual condition, it does not preserve size-extensivity in general. A further, particular delicate issue is revealed by looking at orbital rotations. In theory, the energy is expected to be invariant under separate rotations of occupied, active, and virtual orbitals, but this property is violated by all methods relying on the JM *ansatz*.[21] Since this gives rise to a certain arbitrariness of energies and molecular properties, it is considered a serious problem of JM-based methods. However, it cannot be ruled out that the JM *ansatz* may be employed to formulate a fully orbital-invariant MRCC method. A further problematic feature common to all MRCC methods based on the JM *ansatz* is the linear scaling of the computational cost with the number of reference determinants. This property renders the application of model spaces with more than six or eight electrons close to impossible.

In MRCI theory, an efficient way to reduce the computational cost is provided by the use of internally-contracted wavefunctions.[22] In analogy to that, it has been also tried to set up an internally-contracted (ic) MRCC wavefunction.

While this *ansatz* possesses two distinct advantages over the JM *ansatz*, namely that the number of amplitudes becomes nearly independent of the number of reference determinants and that the cluster operator can be chosen such that full orbital invariance is ensured, it leads to significant complications, too. Due to a more involved structure of the cluster operator $\hat{T}$, the Baker-Campbell-Hausdorff expansion that is in general employed to derive explicit expressions for the cluster amplitudes does not truncate as it does in the case of SRCC and JM-based MRCC wavefunctions, which significantly impedes the implementation of ic-MRCC. Several concepts including automated implementation techniques have been proposed to deal with this issue,[10,23] but a convincing realization of the theory in a production-level code has not yet been presented.

3 Conclusion

In this paper, we have given an overview into MRCC theory. We presented several MRCC approaches currently under consideration and showed that they all violate certain criteria that a convincing MRCC approach is expected to fulfill. Although remarkable progress in the field of MRCC theory has been achieved during the last years and some MRCC methods show reasonably well performance for model applications, it still remains an open question if it is possible to set up a MRCC method satisfying all theoretical criteria discussed. Furthermore, it is unclear if either one of the three presented wavefunction *ansätze* is suited for the formulation of such a method or if a novel *ansatz* is needed. But even if such an optimal MRCC method exists in theory, it needs to deliver significantly better results than SRCC, MR-AQCC and MR-ACPF methods to prevail against the latter. This is not a small hurdle given the often surprisingly good performance of MR-AQCC and MR-ACPF and the well-known ability of SRCC methods to correct for quasi-degeneracy effects by inclusion of higher excitations into the cluster operator. Despite these challenges, we are convinced that the use of genuine MRCC methods repre-

sents the best approach to treat quasi-degeneracy effects at a level of high accuracy and that the formulation of a perfect MRCC *ansatz* is possible.

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