

Exploiting New Advances in Mathematics to Improve Calculations in Quantum Molecular Dynamics

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1 Introduction and Overview of the Field

The main goal of this workshop was to foster communication between chemists developing mathematical and computational tools for studying the motion of atoms in polyatomic molecules and mathematicians interested in numerical methods for high-dimensional problems and in semi-classical mechanics. Scientists in these two groups benefit from talking with one another, and they have traditionally not done communicated well. Often, the two groups have used different terminology for the same thing; sometimes they have developed very similar ideas in parallel. Development of new methods and ideas is facilitated by exchange and interaction among the groups. Although there is a lot of overlap, scientists in the two groups sometimes lose track of the priorities and interests of members of the other group. For this reason also, interaction is important.

Mathematicians studying quantum molecular problems have often concentrated on diatomic molecules and semi-classical methods, while chemists have been interested in larger molecules and new computational tools. To compute properties of molecules with more than three atoms it is necessary to deal with the “curse of dimensionality” because $3N$ coordinates are required to describe the configuration of N particles. Even if one is just studying the motion of the nuclei, a molecule with 5 atoms requires computations in 15 dimensions. Effective computational techniques exist for studying partial differential equations in up to three dimensions, but computations in higher dimensions are harder and have only recently been the focus of attention from mathematicians. This is perhaps due to the fact that most engineering problems are 3D because we live in a 3D world. It is always possible to eliminate, from the $3N$ coordinates, three coordinates associated with the motion of the center of mass. When one is interested in total angular momentum equal to zero ($J = 0$) solutions, it also possible to remove three more coordinates reducing the dimensionality to $3N - 6$. One can easily write down the time-dependent and time-independent Schrödinger equations one would like to solve, but they are very hard to solve because of the typically high dimensionality.

At the workshop, mathematicians and chemists presented new methods for solving Schrödinger equations. There is a lot of overlap. Both mathematicians and chemists are developing generalized surface hopping methods for non-adiabatic dynamics; [31, 13] both mathematicians and chemists are developing sparse grid and sparse basis methods for high-dimensional problems; [28, 1, 2, 3, 26, 35, 36, 17] both mathematicians and chemists are developing methods that exploit the advantages of low-rank tensor representations also for high-dimensional problems; [5, 27] both mathematicians and chemists are developing semi-classical methods [18, 19, 20, 38, 25] that exploit the relatively large masses of nuclei (compared to those of electrons). In Banff there was an exchange about developments that have been achieved so far and some cross fertilization. It helps mathematicians to be told what problems are important in chemistry. It helps chemists to be given rigorous results about what is possible. Chemists have a tendency to explore and test ideas without

analyzing them in detail. Mathematicians are often able to learn from and then render more precise ideas that chemists propose. Algorithms developed by mathematicians are almost always more general than those developed by chemists. At the Banff meeting both sides searched for ways in which ideas of mathematicians can be applied to chemistry.

In many prior conferences and workshops that brought together mathematicians and chemistry working on molecular dynamics, there have been significant difficulties getting chemists and mathematicians to talk to one another in a meaningful way. Differences in nomenclature, aims, and priorities have often been barriers. As stated above, the main goal of this workshop was to facilitate the interaction between the two groups, and in this regard, the workshop was very successful.

2 Recent Developments and Open Problems

2.1 Techniques for High-Dimensional Problems

2.1.1 Methods based on sparse-grid ideas

Both chemists and mathematicians presented talks about recent developments in sparse-grid ideas. The most obvious way to solve a D dimensional differential equation is to use a method that chemists call variational and mathematicians call Galerkin and a product basis. A product (tensor product) basis is one for which each function is a product of functions of a single variable. Such ideas work well in 3 dimensions (*e.g.*, for a molecule with 3 atoms) but fail in 12 dimensions (*e.g.*, for a molecule with 6 atoms). They fail in 12 dimensions because the size of the product basis scales as n^D where n is a representative number of basis functions per coordinate and D is the number of coordinates. Because n is often about 10, n^D is about 10^{12} when $D=12$. On present day computers, it is not possible to even store in memory a vector representing the solution in such a basis. In the last 5 to 10 years chemists and mathematicians have begun to use ideas originally suggested by Smolyak to mitigate problems associated with product basis sets. [37, 16, 15, 10, 23, 32, 4, 14, 17, 40, 39] Many of the prominent people in this field attended the workshop. An open problem in this field is coping with the complicated kinetic energy operators that occur when curvilinear coordinates are used. Another is the difficulty of exploiting molecular symmetry with sparse-grid type methods.

2.1.2 Methods based on using low rank tensor

This is a field in which chemists were far ahead of mathematicians, but mathematicians have caught up quickly. Several of the key people working in this field were also at the workshop. The coefficients that represent a D dimensional wavefunction in a product basis form a D th order tensor. In many cases that tensor can be re-written in terms of tensors of lower order. If, in addition, one can find a way to directly compute the lower order tensors from which one can build the D th order tensor then one has a computational method that enables one to beat the curse of dimensionality. An open problem in this area is linking iterative eigensolvers and propagation methods to tensor methods in such a way that high precision can be achieved. Another open problem is the re-representation of the potential energy surface (PES). [30, 34, 8, 11, 9, 24, 29] Tensor methods cannot be used with general PESs. Many tensor-type methods work only if the PES is a sum-of-products, what mathematicians call CP format. All methods for generating SOP PESs have important deficiencies.

2.2 More Theoretical Issues

2.2.1 Non-adiabatic problems

There are many problems in chemistry for which interactions between different Born-Oppenheimer PESs are important. [18, 25, 38, 21, 6, 7] Both chemists and mathematicians are developing and applying methods to treat such problems. The usual starting point is to assume the nuclear motion on a single PES is determined by classical mechanics and electronic transitions between PESs are determined from the rules of quantum mechanics. It is simply too complicated to use quantum mechanics for the entire problem. The open problem here is improving the approximations that are necessarily introduced in order to patch together quantum and classical mechanics.

2.2.2 Mathematics of Molecular Schrödinger Operators

Molecules have both large mass particles (nuclei) and small mass particles electrons). The usual Born–Oppenheimer approximation employs a semi-classical approximation for the nuclei and an adiabatic approximation for the electrons. Although the paper of Born and Oppenheimer was published in 1927, mathematicians did not begin analyzing the situation until roughly 1980. There has now been substantial mathematical analysis that involves one PES, and there are several papers that deal with several PES's. [18, 25, 38, 22] Many of the authors of those papers attended this workshop.

The simplest non-adiabatic behavior occurs at level crossings, where two PES's intersect. Generically, the most interesting level crossings are “conical intersections,” which require PES's that depend on at least two nuclear coordinates. [18, 12, 38] They do not occur in diatomic molecules. Another closely related situation is an “avoided crossing,” in which two PES's approach very close to one another, but do not actually intersect. There are now a few mathematical papers that deal with that situation. [19, 20, 21, 6, 7]

The technique of “surface hopping” is frequently used in chemistry to study these situations, but there are no mathematically rigorous papers justifying these approximations in general. [33, 31, 13] That is an area which is begging for some mathematical analysis to be done. One would hope that workshops like this one would stimulate mathematical work in such a direction.

In general, the workshop was effective at bringing mathematicians and chemists into discussion. The long coffee breaks were key. One small illustration of the nature of the problem. Two of the participants, Caroline Lasser (mathematician) and Christoph Scheurer (chemist), had never met. This would not be unusual except for the fact that they are from the same university! At the conference they had time to learn about each other's (related) research. In another case a mathematician, George Hagedorn directed a chemist, Daniel Pal  ez–Ruiz, to a mathematician, Stephan de Bi  vre, at Pal  ez–Ruiz's university.

3 Presentation Highlights

Several of the talks concentrated on “tensor methods” for trying to deal with the “curse of dimensionality.” Those speakers included Arnaud Leclerc, Ove Christiansen, Mike Espig, Uwe Manthe, Ivan Oseledets, Reinhold Schneider, Phillip Thomas, and Edward Valeev. Other talks had a different approach that relied on using sparse grids for computations. Those included Gustavo Avila, David Lauverg  at, and Christoph Scheurer. Yet another approach using wavelets was described by Helmut Harbrecht. Other new methods for solving the time-independent Schr  dinger equation were presented by James Brown, Attila Czaszar, Peter Felker, and George Hagedorn. Uwe Manthe talked about the impossibility of factorizing wavefunctions for CH_5^+ .

Several speakers talked about various methods for solving time-dependent Schr  dinger problems. Those included Volker Betz, Victor Batista, Christian Lubich, Vasile Gradinaru, Gabriel Hanna, Ray Kapral, David Sattlegger, Stefan Teufel, and Robert Wodraszka. Other talks dealt with closely related topics involving nuclear motion.

There were presentations on many other topics. For example, Michael Griebel and Daniel Pal  ez–Ruiz talked about efficient representations of electron energy surfaces. Alain Joye and Stephanie Troppmann made presentations related to open quantum systems in which a small system (such as a molecule) interacts with some very large system that is regarded as a reservoir. The talks of Ramond Kapral and Gabriel Hanna also dealt with small systems coupled to large systems.

Tomoki Ohsawa gave a presentation that concentrated on a geometric approach to quantum mechanics. Bill Poirier described a new approach to quantum mechanics. Raymond Kapral talked about surface hopping techniques that were also mentioned in several other talks.

Tucker Carrington, Caroline Lasser, and George Hagedorn talked about specific molecules and used examples to illustrate general techniques.

Johannes Keller talked about “spectrograms,” which are new objects for the study of semi-classical quantum mechanics in phase space. David Tannor and James Brown also talked about phase space methods, and

Jiri Vanicek talked about molecules in external electromagnetic fields. Pierre-Nicholas Roy presented a talk about path integrals.

4 Scientific Progress Made

As indicated in the introduction, the main goal of this workshop was the sharing of information between mathematicians and chemists. Many participants commented that this meeting was more successful than earlier such meetings that brought the two groups of researchers together. The two groups often have closely related goals, but they publish their results in different journals and often one group has no idea of progress made by the other group. The speakers from each group made an effort to address the other group, which often does not happen in such meetings. Also, some speakers welcomed the opportunity to present their work to audiences they had never addressed before.

Both groups gained insight into activities and scientific difficulties encountered by the other group. Quite clearly, the “curse of dimensionality” is of primary concern to people doing calculations, while semi-classical methods are of primary concern to people doing theoretical analysis. Semi-classical methods are appropriate for the dynamics of nuclei because of their large masses (compared to electrons). They can also be useful for large molecules where a full quantum treatment may not be feasible. Also, in problems involving non-adiabatic behavior, one often would like to deal with the nuclear motion easily, since the main emphasis is on understanding what the electrons are doing.

5 Fundamental Open Questions

Mathematical semi-classical analysis is based on either the assumption that \hbar is small or that the ratio of masses is small. In the former case semi-classical approximations work well, and in the latter cases adiabatic approximations are appropriate. Born–Oppenheimer type approximations use both of these approximations, and most of the theory of molecular quantum mechanics is built on the ability to sequentially solve electronic and nuclear Schroedinger equations. Mathematicians are working on ways to improve and correct these approximations. It is important to know whether the corrections enable one to achieve the sort of accuracy desired by chemists. The alternative is to use numerical methods. We need more tests to determine whether savings can be achieved with semi-classical and improved adiabatic approximations, without sacrificing accuracy.

The use of tensor methods in calculations will benefit from more theoretical analysis. We need better rank reduction methods. In the application of Smolyak methods to problems of chemical interest, more work is needed to develop ideas to exploit symmetry. It would also be beneficial to develop good black–box methods that can be used by non–experts.

6 Outcome of the Meeting

The two groups of researchers left the workshop with a better appreciation of the issues dealt with by the other group. Mathematicians are beginning to make important contributions to the development of methods for solving the high dimensional problems that are ubiquitous in chemistry.

References

- [1] G. Avila and T. Carrington, Jr., Nonproduct quadrature grids for solving the vibrational Schrödinger equation. *J. Chem. Phys.* **131** 174103 (2009).
- [2] G. Avila and T. Carrington, Jr., Using nonproduct quadrature grids to solve the vibrational Schrödinger equation in 12D. *J. Chem. Phys.* **134** 054126 (2011).

- [3] G. Avila and T. Carrington, Jr., Using a pruned basis, a non-product quadrature grid, and the exact Watson normal-coordinate kinetic energy operator to solve the vibrational Schrödinger equation for C_2H_4 . *J. Chem. Phys.* **135** 064101 (2011).
- [4] V. Barthelmann, E. Novak, and K. Ritter, High dimensional polynomial interpolation on sparse grids. *Adv. Comput. Math.* **12** 273–288 (2000).
- [5] M. H. Beck, A. Jäckle, G. A. Worth, and H.-D. Meyer, The multiconfiguration time-dependent Hartree (MCTDH) method: a highly efficient algorithm for propagating wavepackets. *Phys. Rep.* **324** 1–105 (2000).
- [6] V. Betz and S. Teufel, Precise coupling terms in adiabatic quantum evolution. *Annales Henri Poincaré* **6** 217–246 (2005).
- [7] Precise coupling terms in adiabatic quantum evolution: The generic case. *Commun. Math. Phys.* **260** 481–509 (2005).
- [8] J. M. Bowman, T. Carrington, and H.-D. Meyer, Variational quantum approaches for computing vibrational energies of polyatomic molecules, *Mol. Phys.* **106** 2145–2182 (2008).
- [9] J. M. Bowman, S. Carter, and X. Huang, A code to calculate rovibrational energies of polyatomic molecules. *Int. Rev. Phys. Chem.* **22** 533–549 (2003).
- [10] H.-J. Bungartz and M. Griebel, Sparse Grids. *Acta Numerica* **13** 147–269 (2004).
- [11] S. Carter, S. J. Culik, and J. M. Bowman, Vibrational self-consistent field method for many-mode systems: A new approach and application to the vibrations of CO adsorbed on Cu(100). *J. Chem. Phys.* **107** 10458–10469 (1997).
- [12] C. Fermanian Kammerer and P. Gérard, Une formule de Landau–Zener pour un croisement générique de codimension 2. *Séminaire Équations aux dérivées partielles 2001-2002* 1-14 (2001-2002).
- [13] C. Fermanian Kammerer, C. Lasser, Single switch surface hopping for molecular dynamics. *J. Math. Chem.* **50** 620–635 (2012).
- [14] M. Griebel and J. Hamaekers, Tensor product multiscale many-particle spaces with finite-order weights for the electronic Schrödinger equation. In M. Dolg, ed., *Modern and Universal First-principles Methods for Many-electron Systems in Chemistry and Physics, volume 3 of Progress in Physical Chemistry*, 237–253, Oldenbourg Wissenschaftsverlag GmbH, München, 2010.
- [15] M. Griebel and S. Knapek, Optimized tensor-product approximation spaces. *Constructive Approximation*, **16** 525–540 (2000).
- [16] M. Griebel and S. Knapek, Optimized general sparse grid approximation spaces for operator equations. *Mathematics of Computations*, **78**, 2223–2257 (2009).
- [17] M. Griebel, M. Schneider, and Ch. Zenger, A combination technique for the solution of sparse grid problems. In *Iterative Methods in Linear Algebra*, R. Beauwens (ed.) P. de Groen (ed.), Elsevier & North-Holland, 263–281 (1992).
- [18] G. A. Hagedorn, Molecular Propagation through Electron Energy Level Crossings. *Memoirs Amer. Math. Soc.* **111** (536), 1–130 (1994).
- [19] G. A. Hagedorn and A. Joye, Landau–Zener Transitions through Small Electronic Eigenvalue Gaps in the BornOppenheimer Approximation. *Ann. Inst. H. Poincaré Sect. A.* **68**, 85–134 (1998).
- [20] G. A. Hagedorn and A. Joye, Molecular Propagation through Small Avoided Crossings of Electronic Energy Levels. *Rev. Math. Phys.* **11**, 41–101 (1999).
- [21] G. A. Hagedorn and A. Joye, Time development of exponentially small non-adiabatic transitions. *Commun. Math. Phys.* **250** 393–413 (2004).

- [22] G. A. Hagedorn and A. Joye, Determination of Non-Adiabatic Scattering Wave Functions in a Born-Oppenheimer Model. *Ann. H. Poincaré* **6**, 937–990 (2005). Erratum **6**, 1197–1199 (2005).
- [23] F. Heiss and V. Winschel, Likelihood Approximation by Numerical Integration on Sparse Grids. *Journal of Econometrics* **144**, 62–80 (2008).
- [24] A. Jäckle and H.-D. Meyer, Product Representation of Potential Energy Surfaces. *J. Chem. Phys.* **104** 7974–7984 (1996).
- [25] C. Lasser and S. Teufel, Propagation through conical crossings: an asymptotic semigroup. *Comm. Pure Appl. Math.* **58** 1188–1230 (2005).
- [26] D. Lauvergnat and A. Nauts, Torsional energy levels of nitric acid in reduced and full dimensionality with ELVIBROT and TNUM *Phys. Chem. Chem. Phys.*, **12** 8405–8412 (2010).
- [27] A. Leclerc and T. Carrington, Jr., Calculating vibrational spectra with sum of product basis functions without storing full-dimensional vectors or matrices. *J. Chem. Phys.* **140** 174111 (2014).
- [28] C. Lubich, *From Quantum to Classical Molecular Dynamics: Reduced Models and Numerical Analysis* (Zurich Lectures in Advanced Mathematics) 2008.
- [29] S. Manzhos and T. Carrington, Jr., Using Neural Networks to Represent Potential Energy Surfaces as Sums of Products. *J. Chem. Phys.* **125** 194105 (2006).
- [30] J. N. Murrell, S. Carter, S. Frantos, P. Huxley, and A. J. C. Varandas, *Molecular Potential Energy Functions*, John Wiley & Sons, Toronto, 1984.
- [31] S. Nielsen, R. Kapral, and G. Ciccotti, Mixed quantum-classical surface hopping dynamics. *J. Chem. Phys.* **112** 6543–6553 (2000).
- [32] E. Novak and K. Ritter, High dimensional integration of smooth functions over cubes. *Numer. Math.* **75**, 79–97 (1996).
- [33] R. K. Preston and J. Tully, Trajectory Surface Hopping Approach to Nonadiabatic Molecular Collisions: The Reaction of H^+ with D_2 . *J. Chem. Phys.* **55** 562–571 (1971).
- [34] H. Rabitz, O. F. Alis, J. Shorter, and K. Shim, Efficient inputoutput model representations *Comput. Phys. Commun.* **117** 11–20 (1999).
- [35] J. I. Rodriguez, D. C. Thompson, J. S. M. Anderson, J. W. Thomson and P. W. Ayers, A physically motivated sparse cubature scheme with applications to molecular density-functional theory. *J. Phys. A: Math. Theor.* **41** 365202 (2008).
- [36] J. I. Rodriguez, D. C. Thompson, P. W. Ayers, and A. Koester, Numerical integration of exchange-correlation energies and potentials using transformed sparse grids. *J. Chem. Phys.* **128** 224103 (2008).
- [37] S. A. Smolyak, Quadrature and interpolation formulas for tensor products of certain classes of functions *Sov. Math. Dokl.* **4**, 240–243 (1963).
- [38] S. Teufel, *Adiabatic Perturbation Theory in Quantum Dynamics*. Lecture Notes in Mathematics 1821. Springer-Verlag, Berlin, Heidelberg, New York, 2003.
- [39] G. W. Wasilkowski and H. Woniakowski, Explicit Cost Bounds for Multivariate Tensor Product Problems. *J. Complexity.* **11** 1–56 (1995).
- [40] H. Yserentant, On the multilevel splitting of finite element spaces. *Numerische Mathematik*, **49** 379–412, (1986).