Remembering John C. Light: II. Scientific Contributions

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In addition to his extensive work as an Editor,[1] John Light published a total of 141 papers on the theory of chemical dynamics in the Journal of Chemical Physics between 1962 and 2007, many of which have had a lasting impact on the way we now do quantum dynamics calculations.

An early highlight of John's work in Chicago in the 1960s was his phase space theory of chemical kinetics,[2,3] and its subsequent development with his graduate student Philip Pechukas into a detailed balance conserving statistical theory of complex-forming reactions.[4,5] This statistical theory has seen a rebirth of interest in the last decade with the help of modern quantum mechanical calculations of the capture probabilities into the collision complex. In conjunction with these capture probabilities, the theory continues to provide a very valuable description of reactions that proceed via deep potential energy wells. In an unrelated project, Pechukas and Light also wrote a classic paper on the Magnus expansion of the time-dependent propagator for problems with time-dependent Hamiltonians.[6] This paper is still attracting the attention of researchers in a variety of different areas, ranging from solid state nuclear magnetic resonance to the dynamics of ions in Paul traps.

In the 1970s, John turned his attention to the exact quantum mechanical solution of the coupled equations of reactive[7] and inelastic[8] scattering, using the R-matrix method. This method, like the log derivative method that was proposed at around the same time by Johnson,[9] avoids the linear dependence problems that are encountered in the presence of closed channels when the scattering wave function matrix is propagated directly. The constant reference potential R-matrix propagator of Stechel, Walker and Light is complementary to the finite difference log derivative propagator of Johnson, and it is to be preferred whenever the potential energy is varying more slowly than the scattering wave function. In fact, the vast majority of the time-independent quantum scattering calculations that have been performed during the last 40 years have used one or other of these two propagators or some improved version of it. John's group performed their first three-dimensional quantum reactive scattering calculation in this way in 1978,[10] followed by a triatomic photodissociation calculation in 1980.[11]

But what is widely regarded as his most significant contribution came in the 1980s, when John and his group introduced the discrete variable representation (DVR).[12-15] This was a truly inspired idea.[16] Before the introduction of the DVR, the standard way to construct a matrix representation of the Hamiltonian was to use a finite basis representation (FBR). This had the advantage that it led to variational upper bounds on energy levels, but the disadvantage that the matrix representation of the potential energy operator was both dense and expensive to compute (especially for high-dimensional problems). In the DVR, the potential energy matrix is diagonal, and it can be computed with an absolute minimum of potential energy evaluations. The kinetic energy matrix is also very easy to compute, and it becomes increasingly sparse for higher dimensional problems. Furthermore, due to its localised nature, the DVR basis can be distributed so as to cover only the energetically accessible regions of the potential energy surface, thereby reducing the basis set size relative to that in the FBR.

The greatest strength of the DVR is undoubtedly its sparsity, which makes it just as easy to use as it is to construct. Vibrational bound state problems can be solved in the DVR using iterative methods such as the Lanczos method, which reduce the diagonalisation of the Hamiltonian matrix to a sequence of sparse matrix-vector multiplications. Inelastic scattering, reactive scattering and photodissociation problems can also be reduced to these operations by adopting the time-dependent wave packet formulation. This can be implemented using a variety of different wave packet propagation techniques, including the elegant and in many cases optimal short iterative Lanczos (SIL) technique that John developed with Tae Jun Park.[17]

Soon after he introduced the DVR, John also suggested using distributed Gaussian basis sets for multidimensional vibrational problems.[18] These basis sets are very flexible, and they have a similar advantage to the DVR in that multi-dimensional potential energy matrix elements are straightforward to evaluate (in this case by low order Gaussian quadrature). However they do not lead to such sparse matrix representations of the Hamiltonian as those obtained in the DVR. So while there has been some interesting further work on distributed Gaussian bases – in particular on those with centres distributed in phase space rather than coordinate space - it is clear that the DVR was the most powerful of all of John's methodological ideas.

Armed with this new methodology, John and his group proceeded to perform some very impressive chemical dynamics calculations that simply would not have been possible using earlier techniques. In the second half of the 1980s, these calculations focused on the highly excited bound (and quasi-bound) states of floppy triatomic molecules and van der Waals complexes,[19-24] which were calculated in the DVR using an efficient sequential diagonalisation/truncation procedure that John developed with Zlatko Bacic. But towards the end of the 1980s, and throughout the 1990s, John returned to his roots as a scattering theorist, making many more applications of his techniques to molecular collision problems, with the help in particular of Dong-Hui Zhang.[25-31] He continued in this vein until his retirement, his final two papers in the journal being on ortho-para hydrogen conversion in the $H_3^+ + H_2$ reaction at collision energies of relevance to the chemistry of the interstellar medium.[32,33] Interestingly, these papers hark back (albeit in a more sophisticated way) to the statistical picture of complex-forming reactions with which he began his career.

John Light was a truly exceptional scientist. He applied the same no nonsense approach to his research as he did to his job as an Editor of the Journal of Chemical Physics. This journal is well known for its papers on theoretical methods and algorithms, but it is rare to see methodological papers of the caliber that John produced himself. The DVR in particular has revolutionised the way we do quantum dynamics calculations, and it is hard to imagine a modern quantum dynamics calculation that does not use this representation in some form or another. The DVR has stood the test of time, and it will continue to do so. Few other methodological developments in chemical physics can claim as much.

1. M. I. Lester, Remembering John C. Light, I. Editorial Contributions, J. Chem. Phys. XX, YYYY (2016).

2. J. C. Light, Phase-space theory of chemical kinetics, J. Chem. Phys. 40, 3221 (1964).

3. J. C. Light and J. Lin, Phase-space theory of chemical kinetics. 2. Ion-molecule reactions, J. Chem. Phys. 43, 3209 (1965).

4. P. Pechukas and J. C. Light, On detailed balancing and statistical theories of chemical kinetics, J. Chem. Phys. 42, 3281 (1965).

5. P. Pechukas, J. C. Light and C. Rankin, Statistical theory of chemical kinetics – Application to neutral atom-molecule reactions, J. Chem. Phys. 44, 794 (1966).

6. P. Pechukas and J. C. Light, On the exponential form of time-displacement operators in quantum mechanics, J. Chem. Phys. 44, 3897 (1966).

7. J. C. Light and R. B. Walker, R matrix approach to solution of coupled equations for atom-molecule reactive scattering, J. Chem. Phys. 65, 4272 (1976).

8. E. B. Stechel, R. B. Walker and J. C. Light, R-matrix solution of coupled equations for inelastic scattering, J. Chem. Phys. 69, 3518 (1978).

9. B. R. Johnson, The multichannel log-derivative method for scattering calculations. J. Comp. Phys. 13, 445 (1973).

10. R. B. Walker, E. B. Stechel and J. C. Light, Accurate H_3 dynamics on an accurate H_3 potential surface, J. Chem. Phys. 69, 2922 (1978).

11. K. C. Kulander and J. C. Light, Photodissociation of triatomic molecules – application of R-matrix propagation methods to the calculation of bound-free Franck-Condon factors, J. Chem. Phys. 73, 4337 (1980).

12. R. W. Heather and J. C. Light, Discrete variable theory of triatomic photodissociation, J. Chem. Phys. 79, 147 (1983).

13. J. C. Light, I. P. Hamilton and J. V. Lill, Generalized discrete variable representation in quantum mechanics, J. Chem. Phys. 82, 1400 (1985).

14. J. V. Lill, G. A. Parker and J. C. Light, The discrete variable finite basis approach to quantum scattering, J. Chem. Phys. 85, 900 (1986).

15. R. M. Whitnell and J. C. Light, Symmetry-adapted discrete variable representations, J. Chem. Phys. 89, 3674 (1988).

16. The FBR to DVR transformation was first introduced by D. O. Harris, G. G. Engerholm and W. D. Gwinn [J. Chem. Phys. 43, 1515 (1965)], who used it as a tool to evaluate potential energy matrix elements in the FBR. A. S. Dickinson and P. R. Certain [J. Chem. Phys. 49, 4209 (1968)] subsequently showed that this was equivalent to evaluating the matrix elements by Gaussian quadrature when the basis was composed of orthogonal polynomials. However, both of these studies were confined to one-dimensional problems, and their focus was on the calculation of the FBR matrix elements. The idea of using the DVR as the *primary* representation, with all of its concomitant advantages in terms of sparsity and locality for high dimensional problems, was John Light's.

17. T. J. Park and J. C. Light, Unitary quantum time evolution by iterative Lanczos reduction, J. Chem. Phys. 85, 5870 (1986).

18. I. P. Hamilton and J. C. Light, On distributed Gaussian bases for simple model multidimensional vibrational problems, J. Chem. Phys. 84, 306 (1986).

19. Z. Bacic and J. C. Light, Highly excited vibrational levels of floppy triatomic molecules – a discrete variable representation – distributed Gaussian basis approach, J. Chem. Phys. 85, 4594 (1986).

20. Z. Bacic and J. C. Light, Accurate localized and delocalized vibrational states of HCN/HNC, J. Chem. Phys. 86, 3065 (1987).

21. Z. Bacic and J. C. Light, Adiabatic approximation and nonadiabatic corrections in the discrete variable representation – highly excited vibrational states of triatomic molecules, J. Chem. Phys. 87, 4008 (1987).

22. Z. Bacic, D. Watt, and J. C. Light, A variational localized representation calculation of the vibrational levels of the water molecule up to 27000 cm^{-1}, J. Chem. Phys. 89, 947 (1988).

23. R. M. Whitnell and J. C. Light, Efficient pointwise representations for vibrational wave functions – eigenfunctions of H_3^+, J. Chem. Phys. 90, 1774 (1989).

24. S. E. Choi and J. C. Light, Determination of the bound and quasi-bound states of Ar-HCl van der Waals complex – discrete variable representation method, J. Chem. Phys. 92, 2129 (1990).

25. T. J. Park and J. C. Light, Quantum flux operators and thermal rate constants – collinear H + H_2, J. Chem. Phys. 88, 4897 (1988).

26. S. E. Choi and J. C. Light, Use of the discrete variable representation in quantum dynamics by a wave packet propagation – Predissociation of NaI, J. Chem. Phys. 90, 2593 (1989).

27. D. H. Zhang and J. C. Light, A six dimensional quantum study for atom triatom reactions: The H+H_2O to H_2+OH reaction, J. Chem. Phys. 104, 4544 (1996).

28. D. H. Zhang and J. C. Light, Cumulative reaction probability via transition state wave packets, J. Chem. Phys. 104, 6184 (1996).

29. D. H. Zhang and J. C. Light, Quantum state-to-state reaction probabilities for the H+H_2O to H_2+OH reaction in six dimensions, J. Chem. Phys. 105, 1291 (1996).

30. D. H. Zhang and J. C. Light, The cumulative reaction probability of the H_2+OH reaction, J. Chem. Phys. 106, 551 (1997).

31. J. Q. Dai and J. C. Light, Six dimensional quantum dynamics study for dissociative adsorption of H_2 on Cu(111) surface, J. Chem. Phys. 107, 1676 (1997).

32. K. Park and J. C. Light, Microcanonical statistical study of ortho-para conversion in the reaction $H_3^+ + H_2$ to H_5^+ to $H_3^+ + H_2$ at very low energies, J. Chem. Phys. 126, 044305 (2007).

33. K. Park and J. C. Light, Nuclear spin selection rules for reactive collision systems by the spin-modification probability method, J. Chem. Phys. 127, 224101 (2007).