THE KWIK ALGORITHM FOR COULOMB INTERACTIONS AND ITS APPLICATIONS

by

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B.Sc.(Hons)

A thesis presented in partial fulfilment
of the requirements for the degree
of Doctor of Philosophy

Department of Chemistry
Massey University
1997

ABSTRACT

The KWIK algorithm is introduced, generalised and applied to the problem of determining the Coulomb energy of N localised charge distributions. Coulomb interactions are typical of N-body problems which require the exhaustive pairing of all distributions, which leads to prohibitive computational cost scaling characteristics for large N.

The KWIK algorithm for Coulomb interactions begins by optimally separating the Coulomb operator into rapidly decaying real- and Fourier- space partitions yielding a hybrid technique not dissimilar in concept to other approximations methods. KWIK's superiority lies is that its efficiency increases with distribution size, so that large distributions become computationally advantageous for increasing accuracy.

Model calculations on a distribution consisting of one million particles using KWIK afforded energies, to high accuracy, within minutes compared with days for quadratic methods. The extension of such a feat to even larger distributions is now limited by machine hardware configurations.

Particular emphasis is placed on the application of the algorithm to Molecular Quantum Mechanics where it is illustrated that the algorithm may be applied to linearise single-point self consistent field calculations. In particular, KWIK can be used to form the Exchange matrix in linear computational cost. This has previously only been achieved by crude approximation techniques and cannot be achieved using Coulomb multipole based methods.

ACKNOWLEDGMENTS

There are many people to whom I owe a great deal of thanks.

Firstly, I offer my sincere thanks to my supervisor Dr Peter M. W. Gill. Peter is a scholar and a gentleman, an outstanding scientist and a friend. He has guided me well throughout the last three years, maintaining an open door (or email) offering clear and well thought out assistance for all problems, and a clever knack for simplifying the complex. His enthusiasm for science, particularly quantum chemistry, has been a great inspiration. Thanks also to the second in command, Dr Ken Jolley, who took over the reins after Peter departed for Cambridge.

There have been others who have aided in increasing my understanding of research, quantum chemistry, mathematics and computing which has had a direct benefit on this thesis. Dr Benny Johnson of Q-Chem Inc., Dr Steve Taylor of the Mathematics Department at the University of Auckland and Chris White, presently at University of California at Berkeley, have been particularly helpful in this regard.

I thank my family for their continued encouragement and support which tends to be required more through difficult times, rather than during the more productive and successful ones. I imagine this thesis will end up on the coffee table as an answer to the question "... and what *exactly is* Jeremy doing at Massey?" continually posed by extended family and visitors.

To the members of Peter's research group who have had to put up with me hacking my way through system administration and bringing workstations to a stand-still with my large scale calculations, I thank you for your patience. Of the group members, Dr Terry Adams is one who has had the largest positive effect on broadening my knowledge and improving my outlook. Thanks Terry for your friendship. I would also like to thank Mrs 'Bot' Gill for many fine lunches and offer my apologies to Malcolm and Stephanie who weren't allowed seconds at dinner time because the remainder was set aside to become my lunch the next day. Thanks also goes to Gwen Adams for providing me with a far superior poster than I could have possibly even attempted to construct for my trip to Paris and Cambridge.

There are also many other friends who have helped maintain a level of sanity (and often reality) outside of Massey whom I have chosen not to name for fear forgetting anyone, or placing them in the incorrect order. I must however, thank Gaile Peddie for putting up with endless sleepless nights, grumpy moods, hogging the phone-line with the modem and general ungentlemanly behaviour, especially during the write-up phase. Past flatmates have also had to suffer through similar agony.

I have been most fortunate in my bids for funding grants and scholarships which allowed me to attend four conferences, three of these international. I offer my humble thanks to the New Zealand Vice Chancellors Committee for a William Georgetti Scholarship and to Massey University for a Doctoral Scholarship. For assistance towards travel to conferences and for computer software, I wish to thank: - Q-Chem Inc., The New Zealand Institute of Chemistry, DFT-95 Conference organisers, Massey University Research Fund, Department of Chemistry, Massey University Graduate Research Fund and the Science Faculty Dean's Fund for generous contributions.

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LIST OF ABBREVIATIONS

1-D	One Dimensional Space
2-D	Two Dimensional Space
3-D	Three Dimensional Space
AO	Atomic Orbital
BLAS	Basis Linear Algebra Subroutines
C++	(object oriented programming language)
CAP	Coulomb Attenuated Potential
CASE	Coulomb Attenuated Schrödinger Equation
CC	Coupled Cluster
CCD	Coupled Cluster with Doubles excitations
CCSD(T)	Coupled Cluster with Singles and Doubles excitations, incorporating Triples perturbatively
CCSDT	Coupled Cluster with Singles, Doubles and Triples excitations
CFMM	Continuous Fast Multipole Method
CI	Configuration Interaction
CISC	Complex Instruction Set Computer
CISD	Configuration Interaction with Singles and Doubles excitations
COP	Coulomb Orthonormal Polynomial
CNDO	Complete Neglect of Differential Overlap
CPU	Central Processing Unit
DE	Differential Equation
DFT	Density Functional Theory
DIIS	Direct Inversion in the Iterative Subspace
ERI	Electron (two) Repulsion Integral
FCI	Full Configuration Interaction
FFT	Fast Fourier Transform
FLOP	Floating Point Operation

FMA	Floating-point Multiply-Add
FMM	Fast Multipole Method
FORTRAN	Formula Translation (programming language)
FT	Fourier Transform
G2	Gaussian-2 theory
GTO	Gaussian type Orbital
GvFMM	Gaussian very Fast Multipole Method
HF	Hartree-Fock
HOMO	Highest Occupied Molecular Orbital
INDO	Intermediate Neglect of Differential Overlap
I/O	Input/Output
KWIK	Name given to the algorithm originally devised by Gill for combinatorial problems which are highly dependent. See Chapter 6 equation (6.9).
LAPACK	Linear Algebra Package
LCAO	Linear Combination of Atomic Orbitals
LHS	Left Hand Side
LUMO	Lowest Unoccupied Molecular Orbital
MA	Multiply-Add
MASPAR	Massively Parallel
MINDO	Modified Intermediate Neglect of Differential Overlap
MO	Molecular Orbital
MOP	Memory Operation
MP	Møller-Plesset
MPn	n^{th}-order Møller-Plesset
MQM	Molecular Quantum Mechanics
NDDO	Neglect of Diatomic Differential Overlap
PC	Personal Computer
PNDO	Partial Neglect of Differential Overlap
PPPM	Particle-Particle-Particle-Mesh

QCI	Quadratic Configuration Interaction
QCID	Quadratic Configuration Interaction with Doubles excitations
QCISD	Quadratic Configuration Interaction with Singles and Doubles excitations
QCISD(T)	Quadratic Configuration Interaction with Singles and Doubles excitations, incorporating Triples perturbatively
RHF	Restricted Hartree-Fock
RHS	Right Hand Side
RISC	Reduced Instruction Set Computer
ROP	Repulsive Orthonormal Polynomial
SCF	Self-Consistent Field
STO	Slater Type Orbital
UHF	Unrestricted Hartree-Fock
WS	Well-Separated

LIST OF PUBLICATIONS

The following papers have been published as a direct consequence of the work undertaken for this thesis:

1. "KWIK: Coulomb Energies in *O*(N) Work." Jeremy P. Dombroski, Stephen W. Taylor and Peter M. W. Gill. *Journal of Physical Chemistry,* (1996) **100**, 6272.

2. "Chemistry without Coulomb Tails." Ross D. Adamson, Jeremy P. Dombroski and Peter M. W. Gill. *Chemical Physics Letters,* (1996) **254**, 329.

3. "The Optimal Partition of the Coulomb Operator." Aaron M. Lee, Stephen W. Taylor, Jeremy P. Dombroski and Peter M. W. Gill. *Physical Review A,* (1997), in press.

NOTE ON CALCULATIONS

All calculations and efficiency developments reported herein, were obtained on an IBM RS/6000 model 355 with 64 MB RAM. All programming was written in FORTRAN 77 and compiled with the IBM XL FORTRAN for AIX compiler, versions 3.2.5 and 4.1.0 with O2 optimisation. Code was linked against the BLAS, LAPACK and Q-CHEM libraries when required.