Australian National University

Applications of Resolutions of the Coulomb Operator in Quantum Chemistry

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A thesis submitted for the degree of
Doctor of Philosophy at the Australian National University

For my parents who teach me the value of education
and do whatever it takes for me to be educated.

For Mahidol Wittayanusorn School and Junior Science Talent Project
which inspired and supported me to pursue a career in science.

Declaration

The work in this thesis is my own except where otherwise stated.

Taweetham Limpanuparb
Canberra, October 2011

Acknowledgements

Though PhD candidates must complete their thesis by themselves, my three-year study in Canberra is not a journey alone. Many individuals and organizations have lent their helping hands to me. Without them, I would not be able to complete the journey towards my PhD.

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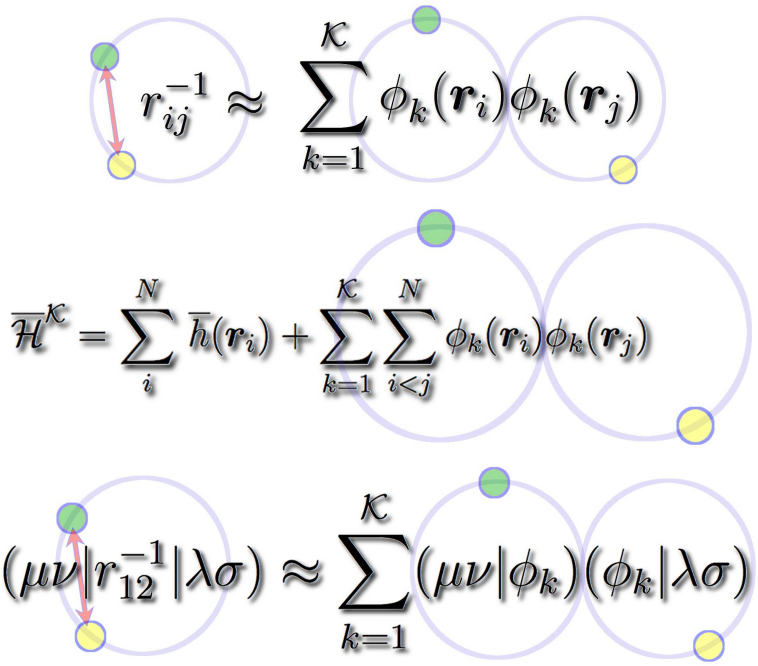
Abstract



This dissertation shows that the Coulomb operator and the long-range Coulomb operators can be resolved as a sum of products of one-particle functions. These resolutions provide a potent new route to tackle quantum chemical problems. Replacing electron repulsion terms in Schrödinger equations by the truncated resolutions yields the reduced-rank Schrödinger equations (RRSE). RRSEs are simpler than the original equations but yield energies with chemical accuracy even for low-rank approximations. Resolutions of the Coulomb operator factorize Coulomb matrix elements to Cholesky-like sums of products of auxiliary integrals. This factorization is the key to the reduction of computational cost of quantum chemical methods.

Contents

Publications and proceedings

This thesis contains materials published in peer-reviewed journals, presented at international conferences and derived from work in collaboration with others. I present these here with contribution declarations. Resolutions of the Coulomb operator is a series of papers. Previous work [1, 2, 3] is reviewed in §2.1.

Publications:

- "Resolutions of the Coulomb operator:
  III. Reduced-rank Schrödinger equations"
  by Taweetham Limpanuparb and Peter M. W. Gill
  published in *Phys. Chem. Chem. Phys.*, 2009, **11** (40), pp 9176–9181 [4]

  This material is presented in Chapter 3. Taweetham Limpanuparb is the principal author and conducted the majority of the research under supervision of Peter M. W. Gill.

- "Resolutions of the Coulomb Operator:
  IV. The Spherical Bessel Quasi-Resolution"
  by Taweetham Limpanuparb, Andrew T. B. Gilbert and Peter M. W. Gill
  published in *J. Chem. Theory Comput.*, 2011, **7** (4), pp 830–833 [5]

  This material is presented in Chapter 4. Taweetham Limpanuparb is the principal author and conducted the majority of the research under supervision of Peter M. W. Gill and Andrew T. B. Gilbert.

- "Resolutions of the Coulomb Operator:
  V. The Long-Range Ewald Operator"
  by Taweetham Limpanuparb and Peter M. W. Gill
  published in *J. Chem. Theory Comput.*, 2011, **7** (8), pp 2353–2357 [6]

  This material is presented in Chapter 5. Taweetham Limpanuparb is the principal author and conducted the majority of the research under supervision of Peter M. W. Gill.

- "A Remarkable Identity Involving Bessel Functions"
  by Diego E. Dominici, Peter M.W. Gill and Taweetham Limpanuparb
  published online at arxiv.org (arXiv:1103.0058v1) [7][1]

  This material is presented in Chapter 7. Taweetham Limpanuparb and Peter M. W. Gill discovered the identity. Introduction, numerical results and concluding remarks sections were written by Taweetham Limpanuparb under supervision of Peter M. W. Gill. Diego E. Dominici provided a proof and wrote preliminaries and main results sections.

Proceedings

- "Resolutions of $1/r_{12}$ and its application in quantum chemistry"
  by Taweetham Limpanuparb and Peter M. W. Gill
  A contributed talk in physical and theoretical chemistry session
  Pure and Applied Chemistry International Conference, Bangkok, 2011

  This material is presented in Chapter 3. Taweetham Limpanuparb conducted the research under supervision of Peter M. W. Gill.

- "Resolving the Coulomb operator:
  A new approach towards faster QM Methods"
  by Taweetham Limpanuparb and Peter M. W. Gill
  A contributed talk in electron correlation theory session
  The 7^{th} Congress of the International Society for Theoretical Chemical Physics, Tokyo, 2011

  This material is presented in Chapter 3 to Chapter 5. Taweetham Limpanuparb conducted the the research under supervision of Peter M. W. Gill.

The structure of scientific manuscript is preserved in chapters mentioned above. However, for clarity and consistency, some parts of the materials were revised, removed or extended to fit the presentation of this thesis.

[1]This was later expanded and submitted to *Proc. R. Soc. A* [10.1098/rspa.2011.0664].

Notation and symbol

In this thesis, we have used the following choice of notation and symbol. Atomic units and real orbitals are used throughout unless otherwise stated.

Notation

a	is a scalar.
a^*	is a complex conjugate of a.
$\|a\|$	is an absolute value of a.
$(a)_n$	is the Pochhammer symbol or rising factorial
$\boldsymbol{a}$	is a vector.
$\|\boldsymbol{a}\|$	is a norm of vector $\boldsymbol{a}$.
$\mathbf{A}$	is a matrix.
$\mathbf{A}^\dagger$	is a conjugate transpose of matrix $\mathbf{A}$.
$\mathbf{I}$	is the identity matrix.
$\mathrm{Tr}[\mathbf{A}]$	is a trace of matrix $\mathbf{A}$.
$\imath$	is the imaginary unit, $\imath^2 = -1$.
$f(r)$	is a function of r.
$\widehat{f}(x)$	is a Fourier transform of $f(r)$.
$\overline{F}$	is an operator.
$\Re(z)$	is the real part of z.
$\Im(z)$	is the imaginary part of z.

Mathematical symbol

$B_z(a,b)$	Incomplete beta function
$\begin{pmatrix} n \\ k \end{pmatrix}$	binomial coefficient
$C_n^{(\lambda)}(z)$	Gegenbauer (or ultraspherical) polynomial
$C_{m,m',m+m'}^{l,l',k}$	Clebsch-Gordan coefficient
$\delta(x)$	Dirac delta function
$\delta_{i,j}$	Kronecker delta
${}_pF_q\left(\begin{matrix} a_1,\ldots,a_p \\ b_1,\ldots,b_q \end{matrix};z\right)$	hypergeometric function
${}_p\tilde{F}_q\left(\begin{matrix} a_1,\ldots,a_p \\ b_1,\ldots,b_q \end{matrix};z\right)$	regularized hypergeometric function
$\Gamma_n(z)$	Gamma function
$H(x)$	Heaviside step function
$H_n(z)$	Hermite polynomial (physicists' Hermite polynomial)
$I(z)$	modified Bessel function of the first kind
$i(z)$	modified spherical Bessel function of the first kind
$J(z)$	Bessel function of the first kind
$j(z)$	spherical Bessel function of the first kind
$L_n(z)$	Laguerre polynomial
$\mathbf{L}_\alpha(z)$	modified Struve function
P_l	Legendre polynomial
$U(x,y)$	parabolic cylinder function
$Y_l^m(\boldsymbol{r})$	complex spherical harmonic
$Y_{lm}(\boldsymbol{r})$	real spherical harmonic

For more comprehensive definition of these symbols, see [8, 9, 10].

Chemical symbol

B	number of basis functions
E	energy
L	angular momentum in basis set
N	number of electrons or normalization constant
ζ	Gaussian basis function's exponent
ω	range-separation parameter
$\rho(\boldsymbol{r})$	electron density
Ψ	wavefunction
φ_μ	atomic orbital
ψ_i	molecular orbital
ε_i	orbital energy
τ	spin variable
$\langle a\|b\rangle$	$\int a^*(\boldsymbol{r})b(\boldsymbol{r})d\boldsymbol{r}$
$\langle a\|\overline{T}\|b\rangle$	$\int\int a^*(\boldsymbol{r}_1)T(\boldsymbol{r}_1,\boldsymbol{r}_2)b(\boldsymbol{r}_2)d\boldsymbol{r}_1 d\boldsymbol{r}_2$

For more comprehensive definition of these symbols, see [11].

Resolution symbol

ϕ_k	resolution function
$\mathcal{N},\mathcal{L},\mathcal{K}$	truncation points of infinite resolution
$\mathcal{Z}$	scaling factor
Δ	logarithm of absolute error of resolution calculation
ϵ	relative error of resolution calculation

For more comprehensive definition of these symbols, see §2.1, §3.3, §4.3 and §5.3.