Resolutions of the Coulomb operator: II. The Laguerre generator

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A B S T R A C T

We discuss a resolution of the Coulomb operator, $r_{12}^{-1} = |\phi_i\rangle\langle\phi_i|$, into a one-particle basis. We show that the Laguerre polynomials generate a resolution with attractive computational properties and we apply it to the calculation of Coulomb and exchange energies in hydrogenic ions, the H_2 molecule, and the Be atom. Rapid convergence is observed in all cases and a theoretical reason for this is discussed.

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1. Introduction

The most troublesome terms in the non-relativistic Schrödinger Hamiltonians for atomic and molecular systems are the two-electron Coulomb operators r_{ij}^{-1}. They are responsible for almost all of the difficulties that confront chemical physicists who seek to understand molecular electronic structure and the reason is simple: it is these terms that are responsible for the coupling of the electrons' motions and which thereby create many-body effects. Life would be much simpler – although life would almost certainly cease to exist – if these terms were removed.

Of course, we are not at liberty simply to drop such terms from our Hamiltonians, but one can ask whether they may be recast into a form that will facilitate both understanding and computation. This is the goal of the present paper and, in particular, we will examine the operator resolution

$$r_{12}^{-1} = |\phi_k\rangle\langle\phi_k| \tag{1}$$

(summation convention implied) and the associated function expansion

$$r_{12}^{-1} = \sum_{k}^{\infty} \phi_k(\mathbf{r}_1)\phi_k(\mathbf{r}_2) \tag{2}$$

which express the Coulomb operator as an infinite sum of binary products of *one*-electron operators.

A corollary of such a resolution is that we can write

$$\langle a|r_{12}^{-1}|b\rangle = \langle a|\phi_k\rangle\langle\phi_k|b\rangle \tag{3}$$

and thus reduce two-electron integrals to sums of products of overlap integrals. This expansion is exact but, if the sum over k is truncated after a finite number of terms, it becomes reminiscent of the low-rank Cholesky [1–3] and Kronecker [4] approximations that are gaining popularity in quantum chemistry. An advantage of our method over other density fitting procedures such as resolution of the identity [5–8] and Poisson fitting [9,10] is that we do not need to compute and manipulate the metric matrix that arises from the interactions between the auxiliary basis functions.

In the early 19th century, a partial resolution was achieved by combining the Legendre expansion with the Addition Theorem for spherical harmonics to find

$$r_{12}^{-1} = \left(r_1^2 + r_2^2 - 2r_1r_2\cos\gamma\right)^{-1/2} = \sum_{l=0}^{\infty} \frac{r_<^l}{r_>^{l+1}} P_l(\cos\gamma)$$

$$= \frac{4\pi}{2l+1} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{r_<^l}{r_>^{l+1}} Y_{lm}(\mathbf{r}_1)Y_{lm}(\mathbf{r}_2) \tag{4}$$

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where γ is the angle between $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$, and $Y_{lm}(\boldsymbol{r})$ is a spherical harmonic [11] of the angular part of $\boldsymbol{r}$. However, although this venerable expansion is very useful, it resolves r_{12}^{-1} into functions of $\boldsymbol{r}_<$ and $\boldsymbol{r}_>$ (the lesser and greater of $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$), rather than $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ themselves.

A decade ago, we observed [12] that another partial resolution can be achieved if the long-range part of the Ewald partition [13]

$$r_{12}^{-1} = \frac{\text{erfc}(\omega r_{12})}{r_{12}} + \frac{\text{erf}(\omega r_{12})}{r_{12}} \tag{5}$$

is expanded in series to yield

$$\frac{\text{erf}(\omega r_{12})}{r_{12}} = \frac{2\omega}{\sqrt{\pi}} \sum_{k=0}^{\infty} \frac{(-\omega^2)^k}{k!(2k+1)} (r_1^2 + r_2^2 - 2\boldsymbol{r}_1 \cdot \boldsymbol{r}_2)^k \tag{6}$$

However, such an expansion is not fully satisfactory because it includes off-diagonal terms and, of course, because the short-range part remains unresolved. A similar partial resolution underpins the KWIK treatment [14–16] of the Coulomb operator.

In a recent communication [17], however, we have presented a more complete solution to the problem, showing that, given a complete set of functions $\{f_k(\boldsymbol{r})\}$ with the Coulomb-orthonormality property

$$\langle f_i | r_{12}^{-1} | f_j \rangle = \delta_{ij} \tag{7}$$

one obtains the Coulomb resolution (1) by choosing the $\phi_k(\boldsymbol{r})$ to be the Coulomb potentials of the $f_k(\boldsymbol{r})$.

We also showed that the functions

$$f_{nlm}(\boldsymbol{r}) = \frac{Y_{lm}(\boldsymbol{r})}{\pi\sqrt{2}} \int_0^{\infty} x^2 h_n(x) j_l(xr) \, dx \tag{8}$$

are complete and Coulomb-orthonormal, if the j_l are spherical Bessel functions [11] and $\{h_n\}$ is a set of functions that are complete and orthonormal on $[0, \infty)$. Moreover, the Coulomb potential of $f_{nlm}(\boldsymbol{r})$ is

$$\phi_{nlm}(\boldsymbol{r}) = 2\sqrt{2} V_{nl}(r) Y_{lm}(\boldsymbol{r}) \tag{9}$$

where the radial potentials are defined by

$$V_{nl}(r) = \int_0^{\infty} h_n(x) j_l(xr) \, dx \tag{10}$$

and comparison with (4) then reveals that

$$\frac{4l+2}{\pi} \sum_{n=0}^{\infty} V_{nl}(r_1) V_{nl}(r_2) = \frac{r_<^l}{r_>^{l+1}} \tag{11}$$

There is an infinite variety of generators $h_n(x)$ and each yields a valid Coulomb resolution (1). In principle, any one of these can be chosen but, in practice, the choice is guided by computational considerations. In [17], we chose the discrete Hermite generator

$$h_n(x) = \frac{(2/\pi)^{1/4}}{2^n \sqrt{(2n)!}} H_{2n}\left(\frac{x}{\sqrt{2}}\right) \exp\left(-\frac{x^2}{4}\right) \tag{12}$$

but this leads to radial potentials that are numerically difficult. Continuous generators are also possible, for example the Dirac generator is

$$h_n(x) = \delta(x - n) \tag{13}$$

where the index n runs over all positive real numbers. The potentials (10) from this generator are simply the spherical Bessel functions

$$V_{nl}(r) = j_l(nr) \tag{14}$$

and the resulting Coulomb resolution is therefore

$$r_{12}^{-1} = 8 \int_0^{\infty} \sum_{lm} j_l(nr_1) Y_{lm}(\boldsymbol{r}_1) j_l(nr_2) Y_{lm}(\boldsymbol{r}_2) \, dn \tag{15}$$

This is elegant but it requires an integration, rather than a sum, over n and is therefore less convenient from a computational point of view. In the present paper, we consider an alternative generator based on the Laguerre polynomials and show that this has several computational advantages. We use atomic units throughout.

2. The Laguerre generator

We define the Laguerre generator to be

$$h_n(x) = \sqrt{2} L_n(2x) \exp(-x) \tag{16}$$

($n = 0, 1, 2, \ldots$) which provides a complete orthonormal set on $[0, \infty)$.

By using the integral representation [11]

$$j_l(z) = \frac{(-i)^l}{2} \int_{-1}^{1} \exp(izt) P_l(t) \, dt \tag{17}$$

(where P_l is a Legendre polynomial), the radial potential (10) can be recast as

$$V_{nl}(r) = \sqrt{2}(-i)^l \frac{z}{2} \int_{-1}^{1} \frac{(-z-t)^n}{(z-t)^{n+1}} P_l(t) \, dt \tag{18}$$

where $z = (ir)^{-1}$. Each potential is a finite sum of elementary functions.

The $l = 0$ potentials are given by

$$V_{n0}(r) = \sqrt{2} \frac{\theta}{r} \left[1 + \sum_{k=1}^{n} (-1)^k \frac{\sin 2k\theta}{k\theta} \right] \tag{19}$$

where $\theta = \tan^{-1} r$. Eq. (19) provides a simple and stable recursive scheme for computing the $V_{n0}(r)$ and Fig. 1 illustrates low-order examples of these.

The $n = 0$ potentials are given by

$$V_{0l}(r) = \sqrt{2} i^l (i/r) Q_l^0(i/r) \tag{20}$$

where Q_l^k is an associated Legendre function of the second kind [11]. These potentials are everywhere non-negative and Fig. 2 illustrates low-order examples of these.

The Laguerre generators (16) and spherical Bessel functions (17) possess the recursive properties [11]

$$\int [h_{n+1}(x) + h_n(x)] \, dx = h_n(x) - h_{n+1}(x) \tag{21}$$

$$(2l+1) \frac{d}{dz} j_l(z) = l j_{l-1}(z) - (l+1) j_{l+1}(z) \tag{22}$$
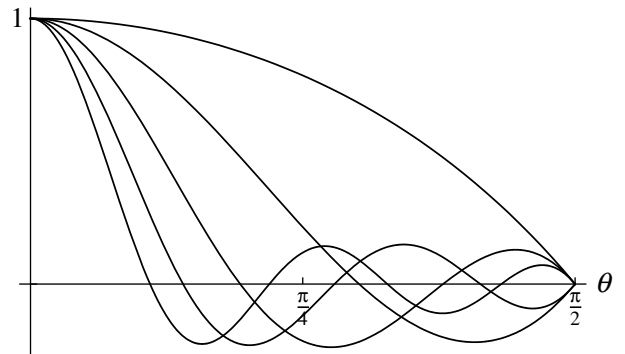
and integration by parts of (10) therefore gives

Fig. 1. $(-1)^n V_{n0}(r)$ for $n = 0, 1, 2, 3, 4$. ($r \equiv \tan\theta$).