Coulomb energies via Stewart densities

Aaron M. Lee, Peter M.W. Gill

Department of Chemistry, University of Cambridge, Cambridge CB2 1EW, UK

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Abstract

We show that the long-range part of the Coulomb self-energy of an electron density $\rho(r)$ is almost identical to that of its associated Stewart density $\tilde{\rho}(r)$. Since the latter is obtained by fitting $\rho(r)$ within an auxiliary basis of only $x$ functions, our proposal can be viewed as a hybrid of the RI (resolution of the identity) and KWIK methods. © 1998 Elsevier Science B.V.

1. Introduction

The main problem bedevilling quantum chemistry is the accurate estimation of the exact electron–electron energy $E_{ee}$ in large systems. Because of instantaneous Coulomb repulsions and the antisymmetry principle, electronic motions are usually strongly correlated and it has proven very difficult to model their behaviour at a reasonable computational cost. The pursuit of such models has fuelled much research in the past and will undoubtedly continue to do so for many years to come. Almost all of the current approaches exploit the fact that $E_{ee}$ rarely differs from $E_J$ by more than a few percent. Thus, on the assumption that $E_J$ can be easily found, the problem is reduced to that of estimating the correction $E_{ee} - E_J$. However, in large systems, even the computation of $E_J$ can become a formidable task and the construction of algorithms that accomplish this as efficiently as possible has attracted research interest for many years.

The early approaches to rapid $E_J$ evaluation were based on the notion that pieces of $\rho(r)$ can be replaced by simple models before the integral Eq. (1) is computed. This idea originated in the work of Boys and Shavitt [1] and resurfaced in the PDDO method of Newton et al. [2], the developments of Harris and Rein [3] and Monkhorst and Harris [4], the LEDO method of Billingsley and Bloor [5] and the VRDDO method of Popkie and Kaufman [6]. In more recent times, it has been revisited by a number of other research groups [7–11].

Two years after the introduction of LEDO, however, Baerends et al. [12] pointed out that it is preferable in some respects to approximate the entire density $\rho(r)$ by a model $\tilde{\rho}(r)$ and compute

$$E_J = \frac{1}{2} \int \frac{\rho(r_1) \rho(r_2)}{r_{12}} dr_1 dr_2. \quad (1)$$

the classical electrostatic self-interaction of the total electron density $\rho(r)$, rarely differs from $E_{ee}$ by more than a few percent. Thus, on the assumption that $E_J$ can be easily found, the problem is reduced to that of estimating the correction $E_{ee} - E_J$. However, in large systems, even the computation of $E_J$ can become a formidable task and the construction of algorithms that accomplish this as efficiently as possible has attracted research interest for many years.

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$$\tilde{E}_J = \frac{1}{2} \int_{\Omega} \tilde{\rho}(r_1) \tilde{\rho}(r_2) dr_1 dr_2. \quad (2)$$

They proposed that $\tilde{\rho}(r)$ be expanded in a relatively small auxiliary basis and constructed by minimizing the integral over all space of the square of the residual $\Delta(r) = \rho(r) - \tilde{\rho}(r)$, i.e. through a least-squares fit. It is easily seen that the quantity to be minimized can be written as

$$Z_i = \int \Delta(r_1) \delta(r_{12}) \Delta(r_2) dr_1 dr_2. \quad (3)$$

and this idea is echoed in later reports by Rys et al. [13] and Yáñez et al. [14], although it does not...
appear that these authors were aware of the work of Baerends. All three of the papers, we note, advocate that charge conservation be added as a constraint to the fitting process.

Subsequently, Dunlap et al. [15] showed that the $E_J$ estimate Eq. (2) is a strict lower bound if one minimizes the self-repulsion

$$Z_2 = \int \int \frac{\Delta(r)}{r_{12}} \Delta(r_2) d r_1 d r_2,$$

(4)

rather than the square, of the residual. As Dunlap et al. discussed, minimizing $Z_2$ corresponds to fitting the electric field, rather than the density, of $\tilde{\rho}(r)$ to that of $\rho(r)$. This new criterion was quickly adopted by the density functional community and has been widely used ever since. It has been systematically explored, and termed the RI-J method, by the Ahlrichs group [16].

It can be shown [17] that one can fit the potential of $\tilde{\rho}(r)$ to that of $\rho(r)$ by minimizing

$$Z_3 = - \int \Delta (r_1) r_{12} \Delta (r_2) d r_1 d r_2,$$

(5)

and that charge conservation arises naturally in this case. This approach, which is related to earlier work by Fortunelli and Salvetti [9], has not yet been exploited. However, the required integrals over the anti-coulomb operator $(-r_{12})$ are straightforward.

One might think that, since they result from different fitting criteria, the model densities obtained by minimizing $Z_1$, $Z_2$ or $Z_3$ would also differ. However, it can be proved [18,19] that, if $\tilde{\rho}(r)$ is constrained to be a sum of $M$ nuclear-centered spherical functions $s_i$, i.e.

$$\tilde{\rho}(r) = \sum \sigma_i |r - R_i|,$$

(6)

the optimal $\sigma_i$ are independent of the fitting criterion and, furthermore, are unique. These robust objects, which we have termed Stewart atoms [19], are difficult to construct exactly but are easily approximated by performing the fit within an auxiliary basis of $s$ functions centered on the nuclei. It follows that the Stewart density is identical to the RI-J density generated by an auxiliary basis that completely spans only the $s$ function subspace.

In the last few years, several quite different approaches to the calculation of $E_J$ have been advanced. Both the CFMM (which uses multipole expansions [20]) and the RBM (which uses recursive bisection [21]) compute $E_J$ in work that scales most linearly with the system size. Another O(N) method, the KWIK algorithm [22], employs the partition

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

(7)

to split $E_J$ into its short-range and long-range components, viz.

$$E_I = E_S + E_L = \frac{1}{2} \langle \rho | S | \rho \rangle + \frac{1}{2} \langle \rho | L | \rho \rangle,$$

(8)

and our group has recently explored several variations on this theme [23–25].

This Letter explores the usefulness of combining the KWIK partition and Stewart theory. Although one might have anticipated that the sphericity of the Stewart atoms would gravely limit the accuracy of the Stewart density, we present results showing that the KWIK-Stewart approximation (KSJ)

$$E_J = E_S + \tilde{E}_L,$$

(9)

in which $E_L$ has been replaced by

$$\tilde{E}_L = \frac{1}{2} \langle \tilde{\rho} | L | \tilde{\rho} \rangle,$$

(10)

generally accurate to a few tens of microhartree per atom if the attenuation parameter $\omega$ is chosen to be 0.4.

2. Method and results

We construct approximate Stewart densities $\tilde{\rho}(r)$ through an expansion in an auxiliary basis of normalized spherically symmetric functions $\phi_i(r)$ centered on the atomic nuclei,

$$\tilde{\rho}(r) = \sum c_i \phi_i(r).$$

(11)

The coefficients in this expansion are then determined by minimizing $Z_2$ in Eq. (4) and satisfy the familiar linear system of equations

$$\sum_i \langle \phi_i | \phi_j \rangle c_i = \langle \phi_j | \rho \rangle,$$

(12)

where

$$\langle f | g \rangle = \frac{1}{2} \int f(r_1) g(r_2) d r_1 d r_2.$$

(13)

A number of choices for the auxiliary basis are...
possible, $s$-type Slater or Gaussian functions, for example. We use even-tempered sequences of uncontracted Gaussians and will investigate other choices elsewhere [26]. The exact Stewart density will be recovered if the auxiliary basis is spherically complete about each nucleus. The restriction to atom-centred spherical functions also ensures that the matrix \( \langle \phi_i | \phi_j \rangle \) will always have full rank. However, for large molecules, \( \langle \phi_i | \phi_j \rangle \) can become near-singular and we therefore use the minimal-norm solution computed using the singular-value-decomposition (SVD) of this matrix. The above theory has been implemented in the Q-Chem[27] package.

We note in passing that it is straightforward to constrain conservation of charge and higher multipole moments into the fitting process, this being facilitated by the SVD which exactly removes any pole moments into the fitting process, this being.

To demonstrate the intrinsic accuracy of the KSJ approximation, we present results using large auxiliary basis sets which we believe to be near the Stewart limit. For all of the molecules examined, we take \( \rho(r) \) to be the UHF/STO-3G density since this facilitates computations on the larger molecules. The parameters \( \alpha, \beta \) and \( n \) for the exponents
\[
\xi_i = \alpha \beta^{-i}, \quad \text{for}\ i = 1, 2, \ldots, n, \tag{14}
\]
in the even-tempered expansions about each nucleus are given in Table 1. For the spherical atoms, these parameters were selected from the range of values giving accurate Coulomb energies (usually to better than 1 part in \( 10^{10} \)) and a suitable range of exponents (errting on the side of diffuseness). The values for the remaining atoms were obtained by interpolation. The long-range energy Eq. (10) of the Stewart density Eq. (11) is easily shown to be
\[
\tilde{E}_L = \frac{1}{2} \sum_{\alpha} \sum_{\gamma} \frac{\text{erf}(R_{st}/\gamma_{st})}{R_{st}}, \tag{15}
\]
where the functions \( \phi_i \) and \( \phi_j \) have exponents \( \alpha_i \) and \( \alpha_j \) on nuclei \( a \) distance \( R_{st} \) apart and
\[
\gamma^{-1} = \alpha_s^{-1} + \alpha_t^{-1} + \omega^{-2}. \tag{16}
\]

<table>
<thead>
<tr>
<th>Nucleus</th>
<th>( n )</th>
<th>( \alpha )</th>
<th>( \beta )</th>
<th>( \xi )</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>20</td>
<td>0.010</td>
<td>1.5</td>
<td>22.1684</td>
</tr>
<tr>
<td>He</td>
<td>20</td>
<td>0.020</td>
<td>1.5</td>
<td>44.3368</td>
</tr>
<tr>
<td>Li</td>
<td>25</td>
<td>0.006</td>
<td>1.5</td>
<td>101.005</td>
</tr>
<tr>
<td>Be</td>
<td>25</td>
<td>0.010</td>
<td>1.5</td>
<td>168.341</td>
</tr>
<tr>
<td>B</td>
<td>25</td>
<td>0.015</td>
<td>1.5</td>
<td>253.512</td>
</tr>
<tr>
<td>C</td>
<td>25</td>
<td>0.020</td>
<td>1.5</td>
<td>336.682</td>
</tr>
<tr>
<td>N</td>
<td>25</td>
<td>0.030</td>
<td>1.5</td>
<td>505.023</td>
</tr>
<tr>
<td>O</td>
<td>25</td>
<td>0.040</td>
<td>1.5</td>
<td>673.364</td>
</tr>
<tr>
<td>F</td>
<td>25</td>
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<td>1.5</td>
<td>842.706</td>
</tr>
<tr>
<td>Ne</td>
<td>25</td>
<td>0.060</td>
<td>1.5</td>
<td>1010.05</td>
</tr>
<tr>
<td>Na</td>
<td>30</td>
<td>0.010</td>
<td>1.5</td>
<td>1278.34</td>
</tr>
<tr>
<td>Mg</td>
<td>30</td>
<td>0.015</td>
<td>1.5</td>
<td>1917.51</td>
</tr>
<tr>
<td>Al</td>
<td>30</td>
<td>0.015</td>
<td>1.5</td>
<td>1917.51</td>
</tr>
<tr>
<td>Si</td>
<td>30</td>
<td>0.020</td>
<td>1.5</td>
<td>2556.68</td>
</tr>
<tr>
<td>P</td>
<td>30</td>
<td>0.025</td>
<td>1.5</td>
<td>3195.85</td>
</tr>
<tr>
<td>S</td>
<td>30</td>
<td>0.030</td>
<td>1.5</td>
<td>3835.02</td>
</tr>
<tr>
<td>Cl</td>
<td>30</td>
<td>0.035</td>
<td>1.5</td>
<td>4474.19</td>
</tr>
<tr>
<td>Ar</td>
<td>30</td>
<td>0.040</td>
<td>1.5</td>
<td>5113.36</td>
</tr>
</tbody>
</table>

We are now in position to analyze the accuracy of the KSJ approximation. Tables 2–4 contain the total Coulomb energies \( E_j \) and both their exact \( E_j \) and approximate \( \tilde{E}_L \) long-range components for a number of chemical systems. We consider two values of the attenuator: \( \omega = 0.4 \), for which \( E_j \) as a fraction of \( E_j \) varies from around 30% to over 90%, and \( \omega = \infty \) where we are approximating all of the Coulomb energy and hence \( E_j = E_j \). The tables also contain the total error in the Coulomb energy \( \Delta E_j = E_j - \tilde{E}_j \) and the error per atom \( \Delta E/J/N_{\text{atom}} \). The short-range component \( E_s \) is computed exactly, in work that grows linearly with the system size, and makes no contribution to the total error in the Coulomb energy. We are guided in our interpretation of these results by the criterion of Eichkorn et al. [16] that approximations to \( E_j \) for molecules should yield an error no greater than 0.2 \( mE_0/\text{atom} \). Accordingly, the results in each table are listed in order of increasing error per atom for the more interesting case with \( \omega = 0.4 \).

Table 2 contains Coulomb energies for a number of small inorganic molecules taken from the G2 set [28] and reveals that the KSJ approximation yields total errors that vary between 1–50 millihartree per atom when we are approximating all of \( E_j \) (\( \omega = \infty \)).
It appears, then, that applying the KWIK-Stewart approximation to $E_J$ as a whole will not yield chemically useful results, which is perhaps to be expected considering that replacing a density by a sum of atomic-centred spherical fragments is a significant approximation. Turning to the $\omega = 0.4$ results, where for these molecules we are treating roughly half of the Coulomb energy exactly, we observe that the quality of the KSJ approximation improves dramatically, in some cases by several orders of magnitude. Diatomic molecules fare particularly badly with errors typically in excess of 1 m $E_r$/atom, well above the 0.2 m $E_r$/atom limit set by Eichkorn et al. [16]. Perhaps surprisingly, the least satisfactory of the molecules examined is Li$_2$, with an error of 3.84 m $E_r$/atom (compared to 0.03 m $E_r$/atom for H$_2$), a clear indication that the $p$-orbital contribution to bonding strongly perturbs the sphericity of the constituent Li atoms. For molecules such as F$_2$ and O$_2$, the asphericity of the atoms is reduced in the former case and enhanced in the latter upon diatomic formation. For highly polar molecules such as FH, we see an overall reduction in the error per atom with the formation of closed shells.
around the nuclei leading to near-spherical environments: the error in an isolated F atom is 0.212 m
\(E_h\) which is reduced to 0.006 m
\(E_r\) atom in the FH molecule. The majority of the remaining molecules are treated accurately with an error around a few tens of microhartree, the tetrahedral molecules heading this list.

A final point of interest in Table 2 is the negative error obtained for CF and SiF. For an incomplete basis
\(E_h\) is a lower bound to
\(E_r\). This is not the case, however, for finite values of \(\omega\) if the operator used in performing the fit is different from that to used to compute the Coulomb energy, in this case \(L(r_{ij}).\) For complete basis sets, the Stewart atom coefficients are independent of the fitting operator and negative values for \(\Delta E_f\) may thus be considered a measure of the degree of incompleteness of the auxiliary basis set. It is, however, a straightforward matter to solve Eq. (12) using the long-range operator to recover the strict inequality
\(E_h \leq E_r\) if this is required.

To examine the effect of increasing molecular

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Formula</th>
<th>(\omega = 0.4)</th>
<th>(\omega = \infty)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(_6)H(_6)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(_6)H(_8)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(_4)H(_6)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4

Coulomb energies \(E_j\) in hartree for a number of large organic molecules with the corresponding long-range component \(E_L\) and its KWIK-Stewart approximation \(\tilde{E}_L\) under partial \((\omega = 0.4)\) and complete \((\omega = \infty)\) attenuation. The total error \(\Delta E_j\) and error per atom \(\Delta E_j/N_{\text{atom}}\) are given in millihartree.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Formula</th>
<th>(\omega = 0.4)</th>
<th>(\omega = \infty)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cholesterol</td>
<td>C(<em>{27})H(</em>{45})O</td>
<td>3307.0033</td>
<td>2852.7754</td>
</tr>
<tr>
<td>Testosterone</td>
<td>C(<em>{19})H(</em>{29})O(_2)</td>
<td>2247.2965</td>
<td>1893.2706</td>
</tr>
<tr>
<td>Taxol</td>
<td>C(<em>{47})H(</em>{31})NO(_{14})</td>
<td>11861.626</td>
<td>10701.891</td>
</tr>
<tr>
<td>Heroin</td>
<td>C(<em>{21})H(</em>{13})NO(_3)</td>
<td>3260.7001</td>
<td>2767.7009</td>
</tr>
<tr>
<td>Penicillin</td>
<td>C(<em>{16})H(</em>{16})N(_2)O(_5)S</td>
<td>2779.1719</td>
<td>2235.8709</td>
</tr>
<tr>
<td>Diazepam</td>
<td>C(<em>{18})H(</em>{31})ClN(_3)O</td>
<td>2186.3009</td>
<td>1717.1043</td>
</tr>
<tr>
<td>Caffeine</td>
<td>C(_{10})H(_10)N(_2)O(_2)</td>
<td>1253.2622</td>
<td>982.53597</td>
</tr>
<tr>
<td>Streptomycin</td>
<td>C(<em>{45})H(</em>{51})N(_2)O(_12)</td>
<td>6456.9266</td>
<td>5622.6971</td>
</tr>
<tr>
<td>Azidothymidine</td>
<td>C(_{10})H(_13)N(_4)O</td>
<td>1937.5162</td>
<td>1556.4304</td>
</tr>
</tbody>
</table>
size, we have computed Coulomb energies for homo-
logous sequences of hydrocarbons and present
these results in Table 3. We consider linear alkanes
(C\textsubscript{\textit{n}}H\textsubscript{\textit{2n}+2}, \textit{r}_{CH} = 1.09 Å, \textit{r}_{CC} = 1.40 Å),
graphite sheets (C\textsubscript{\textit{6n}}H\textsubscript{\textit{6n}}, \textit{r}_{CH} = 1.09 Å, \textit{r}_{CC} = 1.42 Å) and
diamond clusters (C\textsubscript{(\textit{4n}−\textit{n})/3}H\textsubscript{\textit{4n}+\textit{n}}, \textit{r}_{CH} = 1.09 Å, \textit{r}_{CC} = 1.54 Å), these sys-

tems exhibiting effective dimensionalities of one,
two and three, respectively. For all of these hydrocarbons the \textit{\omega} = \infty results are dismal,
but again we see a dramatic improvement on moving
to \textit{\omega} = 0.4. From this table, it is clear that \textit{E}\textsubscript{\textit{J}}
increases roughly linearly with system size for the
1D systems, as we would expect, and thus \Delta \textit{E}_{\textit{J}}/N\text{\textsubscript{atom}}
tends to a roughly constant value which, for \textit{\omega} = 0.4,
is around 12 \mu\textit{E}_{\text{h}}/\text{atom}. The sub-quadratic increase
in the magnitude of \textit{E}_{\textit{J}} for the 2D and 3D systems
implies that \Delta \textit{E}_{\textit{J}}/N\text{\textsubscript{atom}} should steadily decrease,
although this is only evident in the \omega = 0.4 results.

Whilst these molecules are somewhat artificial, it is
nonetheless pleasing that we obtain an error less than
15 \mu\textit{E}_{\text{h}}/\text{atom} whilst approximating around 90% of
\textit{E}_{\text{J}} for the larger molecules, a proportion which
increases with system extent.

We conclude our analysis of the KSJ approxima-
tion by studying a variety of biomolecules \textsuperscript{1} and
give these results in Table 4. In the \textit{\omega} = 0.4 results
we have found a clear correlation between the num-
ber and nature of the functional groups and the error
in \textit{E}_{\text{K}}. The azido group appears alone to lead to an
error of around 2 millihartree (compare the error for
N\textsubscript{2} in Table 2). Errors of around 0.4 \mu\textit{E}_{\text{h}} result from
other multiply bonded functional groups such as
carbonyls and smaller, but significant, errors from
ether and amino fragments. This ‘functional group
error’ is approximately additive because the interac-
tion error between well-separated aspherical nuclei is
primarily dipolar and thus vanishes like \textit{R}\textsuperscript{−3}. De-
spite this systematic error, the highly accurate treat-
ment of the hydrocarbon backbone means that for all
of the molecules in this table we are well within the
Eichkorn criterion of 0.2 \mu\textit{E}_{\text{h}}/\text{atom}. These results
suggest that the KSJ approximation is an excellent
route to obtaining accurate Coulomb energies for
medium to large biological systems.

\textbf{3. Conclusions}

We have explored the proposal that long-range
Coulombic interactions can be treated accurately
through a representation of the density as a sum of
spherical nuclear-centred fragments. We observe that
for many systems of interest, such as large organic
molecules, this approximation leads to errors that are
well within the Eichkorn criterion of 0.2 \mu\textit{E}_{\text{h}}/\text{atom}.

We have further shown that the errors resulting from
use of this approximation are systematic and can be
rationalized.

This approach is based on an unusually simple
auxiliary basis and depends only on integrals that can be
computed extremely rapidly. Although we have not
considered the optimization of the auxiliary basis set
in this work, deferring this to future studies \textsuperscript{26}, we
believe that quite compact basis sets will yield errors
close to the Stewart limit. Combined with the effi-
cient computation of \textit{E}_{\text{K}} \textsuperscript{29}, the KWIK-Stewart
approximation promises to be one of the most effi-
cient methods available for the computation of the
Coulomb energy in large systems.

A disadvantage of the KSJ approximation is that
its errors cannot be systematically reduced as in
other fitting techniques by driving the auxiliary basis
set to completeness. The preliminary results obtained
in this Letter demonstrate nonetheless that the KSJ
approximation is sufficiently accurate to merit use on
its own or as a springboard to more accurate computa-
tions.

\textbf{Acknowledgements}

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DMI-9460396).

\textbf{References}

\begin{itemize}
\item [1] S.F. Boys, I. Shavitt.
(1968) 5192.
\end{itemize}

\textsuperscript{1} The geometries of these molecules are available on request.