

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 $\rho(\mathbf{r})$ is almost identical to that of its associated Stewart density $\tilde{\rho}(\mathbf{r})$. Since the latter is obtained by fitting $\rho(\mathbf{r})$ within an auxiliary basis of only s 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

$$E_J = \frac{1}{2} \iint \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2, \quad (1)$$

the classical electrostatic self-interaction of the total electron density $\rho(\mathbf{r})$, 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 be 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 $\rho(\mathbf{r})$ 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 Monkhurst 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 $\rho(\mathbf{r})$ by a model $\tilde{\rho}(\mathbf{r})$ and compute

$$\tilde{E}_J = \frac{1}{2} \iint \frac{\tilde{\rho}(\mathbf{r}_1)\tilde{\rho}(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2. \quad (2)$$

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

$$Z_1 = \iint \Delta(\mathbf{r}_1) \delta(r_{12}) \Delta(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2, \quad (3)$$

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

$$Z_2 = \iint \frac{\Delta(\mathbf{r}_1)\Delta(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2, \quad (4)$$

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 $\tilde{\rho}(\mathbf{r})$ to that of $\rho(\mathbf{r})$. 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 $\tilde{\rho}(\mathbf{r})$ to that of $\rho(\mathbf{r})$ by minimizing

$$Z_3 = - \iint \Delta(\mathbf{r}_1) r_{12} \Delta(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (5)$$

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 $\tilde{\rho}(\mathbf{r})$ is constrained to be a sum of M nuclear-centered spherical functions, *i.e.*

$$\tilde{\rho}(\mathbf{r}) = \sum_j \sigma_j (|\mathbf{r} - \mathbf{R}_j|), \quad (6)$$

the optimal σ_j 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 al-

most linearly with the system size. Another O(N) method, the KWIK algorithm [22], employs the partition

$$r_{12}^{-1} \equiv S(r_{12}) + L(r_{12}) = \frac{\text{erfc}(\omega r_{12})}{r_{12}} + \frac{\text{erf}(\omega r_{12})}{r_{12}} \quad (7)$$

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

$$E_J \equiv E_S + E_L = \frac{1}{2} \langle \rho | S | \rho \rangle + \frac{1}{2} \langle \rho | L | \rho \rangle, \quad (8)$$

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)

$$E_J \approx E_S + \tilde{E}_L \quad (9)$$

in which E_L has been replaced by

$$\tilde{E}_L = \frac{1}{2} \langle \tilde{\rho} | L | \tilde{\rho} \rangle, \quad (10)$$

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

2. Method and results

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

$$\tilde{\rho}(\mathbf{r}) = \sum_s c_s \phi_s(\mathbf{r}). \quad (11)$$

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

$$\sum_t \langle \phi_s | \phi_t \rangle c_t = \langle \phi_s | \rho \rangle, \quad (12)$$

where

$$\langle f | g \rangle \equiv \frac{1}{2} \iint \frac{f(\mathbf{r}_1) g(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2. \quad (13)$$

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 $\langle \phi_s | \phi_t \rangle$ will always have full rank. However, for large molecules, $\langle \phi_s | \phi_t \rangle$ 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 null constraints. However, our investigations showed that a substantial degradation in accuracy resulted when charge or charge + dipole constraints were imposed and we therefore do not recommend the constrained solution of the fitting equations Eq. (12).

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 $\rho(\mathbf{r})$ to be the UHF/STO-3G density since this facilitates computations on the larger molecules. The parameters α , β and n for the exponents

$$\zeta_i = \alpha \beta^{i-1}, \quad \text{for } i = 1, 2, \dots, n, \quad (14)$$

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 (erring 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

$$\tilde{E}_L = \frac{1}{2} \sum_{st} c_s c_t \frac{\text{erf}(R_{st} \sqrt{\gamma_{st}})}{R_{st}}, \quad (15)$$

where the functions ϕ_s and ϕ_t have exponents α_s and α_t on nuclei a distance R_{st} apart and

$$\gamma^{-1} = \alpha_s^{-1} + \alpha_t^{-1} + \omega^{-2}. \quad (16)$$

Table 1

Even-tempering parameters α and β and basis set dimensions n for atoms H through Ar

Nucleus	n	α	β	ζ_n
H	20	0.010	1.5	22.1684
He	20	0.020	1.5	44.3368
Li	25	0.006	1.5	101.005
Be	25	0.010	1.5	168.341
B	25	0.015	1.5	253.512
C	25	0.020	1.5	336.682
N	25	0.030	1.5	505.023
O	25	0.040	1.5	673.364
F	25	0.050	1.5	842.706
Ne	25	0.060	1.5	1010.05
Na	30	0.010	1.5	1278.34
Mg	30	0.015	1.5	1917.51
Al	30	0.015	1.5	1917.51
Si	30	0.020	1.5	2556.68
P	30	0.025	1.5	3195.85
S	30	0.030	1.5	3835.02
Cl	30	0.035	1.5	4474.19
Ar	30	0.040	1.5	5113.36

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_L 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_L 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 $E_L = E_J$. The tables also contain the total error in the Coulomb energy $\Delta E_J = E_L - \tilde{E}_L$ 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 $0.2 m E_h / \text{atom}$. 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 ($\omega = \infty$).

Table 2

Coulomb energies E_J in hartree for a number of small molecules from the G2 set with the corresponding long-range component E_L and its KWIK-Stewart approximation \tilde{E}_L under partial ($\omega = 0.4$) and complete ($\omega = \infty$, $E_L = E_J$) attenuation. The total error ΔE_J and error per atom $\Delta E_J/N_{\text{atom}}$ are given in millihartree

Molecule	E_J	$\omega = 0.4$				$\omega = \infty$		
		E_L	\tilde{E}_L	ΔE_J	$\Delta E_J/N_{\text{atom}}$	\tilde{E}_L	ΔE_J	$\Delta E_J/N_{\text{atom}}$
CF ₄	422.58937	254.57753	254.57756	−0.033	−0.007	422.52117	68.2	13.6
SiF ₄	603.77286	347.95265	347.95266	−0.013	−0.003	603.72868	44.2	8.84
CH ₄	32.797013	17.308532	17.308529	0.003	0.0006	32.793848	3.16	0.63
BF ₃	273.77420	151.22640	151.22639	0.012	0.003	273.74265	31.6	7.89
SiH ₄	155.44513	56.840188	56.840167	0.022	0.004	155.44051	4.62	0.92
CO ₂	148.06763	77.855652	77.855636	0.016	0.005	148.04129	26.3	8.78
FH	56.559401	20.200339	20.200326	0.013	0.006	56.532766	26.6	13.3
AlF ₃	426.90967	227.37462	227.37457	0.046	0.011	426.88039	29.3	7.32
OH ₂	47.222396	19.345861	19.345806	0.055	0.018	47.188338	34.1	11.4
SiCl ₄	1463.9758	774.22461	774.22448	0.134	0.027	1463.9547	21.1	4.22
H ₂	1.3505936	0.7394646	0.7394025	0.062	0.031	1.3484373	2.16	1.08
BCl ₃	847.24990	396.27862	396.27846	0.160	0.040	847.23568	14.2	3.55
NH ₃	39.332677	18.391612	18.391449	0.164	0.041	39.307590	25.1	6.27
AlCl ₃	1018.2779	491.62945	491.62925	0.193	0.048	1018.2676	10.3	2.58
CCl ₄	1262.8479	658.82511	658.82482	0.286	0.057	1262.8120	35.9	7.17
H ₂ CO	86.434219	43.935834	43.935424	0.410	0.10	86.396225	38.0	9.50
HCN	67.813143	34.108114	34.107802	0.312	0.10	67.793686	19.5	6.49
F ₂	130.95320	58.486805	58.486542	0.264	0.13	130.86236	90.8	45.4
SH ₂	192.55942	61.532249	61.531781	0.468	0.16	192.53523	24.2	8.06
PH ₃	173.27377	59.206223	59.205319	0.904	0.23	173.25296	20.8	5.20
BeH	9.5330786	4.2875370	4.2868215	0.715	0.36	9.5235499	9.53	4.76
O ₂	100.34836	46.570055	46.569025	1.03	0.52	100.29550	52.9	26.4
SO	260.31646	101.51079	101.50915	1.64	0.82	260.28023	36.2	18.1
PF ₃	494.23202	262.85622	262.85219	4.03	1.01	494.13682	95.2	23.8
LiH	5.7344206	2.6690799	2.6669833	2.10	1.05	5.7248484	9.57	4.79
S ₂	429.09813	167.04298	167.04082	2.16	1.08	429.07238	25.8	12.9
N ₂	73.978539	35.397098	35.394824	2.27	1.14	73.931405	47.1	23.6
P ₂	373.70555	146.12461	146.12229	2.32	1.16	373.68972	15.8	7.92
Cl ₂	479.09723	185.77623	185.77388	2.35	1.17	479.03569	61.5	30.8
CO	76.415321	35.571591	35.568669	2.92	1.46	76.363695	51.6	25.8
Si ₂	315.84689	121.59752	121.59224	5.28	2.64	315.81600	30.9	15.5
Li ₂	10.375392	4.9415362	4.9338534	7.68	3.84	10.357926	17.5	8.73

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_h /atom, well above the 0.2 m E_h /atom limit set by Eichkorn et al. [16]. Perhaps surprisingly, the least satisfactory of the molecules examined is Li₂, with an error of 3.84 m E_h /atom (compared to 0.03 m E_h /atom for H₂), a clear indication that the p -orbital contribution to bonding strongly perturbs the sphericity of the constituent Li atoms. For molecules such as F₂ and O₂, 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

Table 3

Coulomb energies E_J in hartree for 1D, 2D and 3D systems of hydrocarbons with the corresponding long-range component E_L and its KWIK-Stewart approximation \tilde{E}_L under partial ($\omega = 0.4$) and complete ($\omega = \infty$, $E_L = E_J$) attenuation. The total error ΔE_J and error per atom $\Delta E_J/N_{\text{atom}}$ are given in millihartree

Molecule	E_J	$\omega = 0.4$				$\omega = \infty$		
		E_L	\tilde{E}_L	ΔE_J	$\Delta E_J/N_{\text{atom}}$	\tilde{E}_L	ΔE_J	$\Delta E_J/N_{\text{atom}}$
C_5H_{12}	292.49985	210.27318	210.27294	0.23	0.014	292.48479	15	0.89
$\text{C}_{10}\text{H}_{22}$	749.82993	583.77215	583.77177	0.38	0.012	749.80183	28	0.88
$\text{C}_{20}\text{H}_{42}$	1863.9000	1530.1783	1530.1776	0.74	0.012	1863.8457	54	0.87
$\text{C}_{40}\text{H}_{82}$	4497.1897	3828.1401	3828.1386	1.44	0.012	4497.0831	107	0.87
$\text{C}_{80}\text{H}_{162}$	10579.864	9240.1586	9240.1558	2.85	0.012	10579.653	211	0.87
C_6H_6	310.65092	219.86540	219.86525	0.15	0.013	310.63878	12	1.01
$\text{C}_{24}\text{H}_{12}$	2263.5739	1893.9009	1893.9008	0.14	0.004	2263.5369	37	1.03
$\text{C}_{54}\text{H}_{18}$	7412.3316	6575.7159	6575.7157	0.19	0.003	7412.2565	75	1.04
$\text{C}_{96}\text{H}_{24}$	17313.459	15821.861	15821.861	0.25	0.002	17313.332	127	1.06
$\text{C}_{10}\text{H}_{16}$	783.44774	624.50438	624.50430	0.08	0.003	783.42748	20	0.78
$\text{C}_{35}\text{H}_{36}$	5232.3508	4668.7443	4668.7443	0.03	0.0005	5232.2939	57	0.80
$\text{C}_{84}\text{H}_{64}$	20613.710	19251.850	19251.850	−0.02	−0.0001	20613.588	122	0.82

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 $0.006 m E_h/\text{atom}$ 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_4 and SiF_4 . For an incomplete basis $\tilde{E}_L(\omega = \infty)$ is a lower bound to $E_L(\omega = \infty)$. This is not the case, however, for finite values of ω

if the operator used in performing the fit is different from that to used to compute the Coulomb energy, in this case $L(r_{12})$. For complete basis sets, the Stewart atom coefficients are independent of the fitting operator and negative values for ΔE_J 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 $\tilde{E}_L \leq E_L$ if this is required.

To examine the effect of increasing molecular

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 ($\omega = \infty$, $E_L = E_J$) attenuation. The total error ΔE_J and error per atom $\Delta E_J/N_{\text{atom}}$ are given in millihartree

Molecule	Formula	E_J	$\omega = 0.4$				$\omega = \infty$		
			E_L	\tilde{E}_L	ΔE_J	$\Delta E_J/N_{\text{atom}}$	\tilde{E}_L	ΔE_J	$\Delta E_J/N_{\text{atom}}$
Cholesterol	$\text{C}_{27}\text{H}_{46}\text{O}$	3307.0033	2852.7754	2852.7749	0.5	0.007	3306.9015	102	1.4
Testosterone	$\text{C}_{19}\text{H}_{28}\text{O}_2$	2247.2965	1893.2706	1893.2700	0.6	0.013	2247.1831	113	2.3
Taxol	$\text{C}_{47}\text{H}_{51}\text{NO}_{14}$	11861.626	10701.891	10701.888	2.7	0.024	11861.066	560	5.0
Heroin	$\text{C}_{21}\text{H}_{23}\text{NO}_5$	3260.7001	2767.7009	2767.6992	1.7	0.034	3260.4612	239	4.8
Penicillin	$\text{C}_{16}\text{H}_{18}\text{N}_2\text{O}_4\text{S}$	2779.1719	2235.8709	2235.8692	1.7	0.043	2778.9728	199	4.9
Diazepam	$\text{C}_{16}\text{H}_{13}\text{ClN}_2\text{O}$	2186.3009	1717.1043	1717.1029	1.4	0.044	2186.1797	121	3.7
Caffeine	$\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$	1253.2622	982.53597	982.53472	1.3	0.052	1253.1290	133	5.6
Streptomycin	$\text{C}_{21}\text{H}_{41}\text{N}_7\text{O}_{12}$	6456.9266	5622.6971	5622.6910	6.1	0.075	6456.2410	686	8.5
Azidothymidine	$\text{C}_{10}\text{H}_{13}\text{N}_5\text{O}_4$	1937.5162	1556.4304	1556.4278	2.7	0.081	1937.1443	372	11.6

size, we have computed Coulomb energies for homologous sequences of hydrocarbons and present these results in Table 3. We consider linear alkanes (C_nH_{2n+2} , $r_{CH} = 1.09$ Å, $r_{CC} = 1.40$ Å), graphite sheets ($C_{6n^2}H_{6n}$, $r_{CH} = 1.09$ Å, $r_{CC} = 1.42$ Å) and diamond clusters ($C_{(4n^3-n)/3}H_{4n^2}$, $r_{CH} = 1.09$ Å, $r_{CC} = 1.54$ Å), these systems exhibiting effective dimensionalities of one, two and three, respectively. For all of these hydrocarbons the $\omega = \infty$ results are dismal, but again we see a dramatic improvement on moving to $\omega = 0.4$. From this table, it is clear that E_J increases roughly linearly with system size for the 1D systems, as we would expect, and thus $\Delta E_J/N_{\text{atom}}$ tends to a roughly constant value which, for $\omega = 0.4$, is around $12 \mu E_h/\text{atom}$. The sub-quadratic increase in the magnitude of E_J for the 2D and 3D systems implies that $\Delta E_J/N_{\text{atom}}$ 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 $15 \mu E_h/\text{atom}$ whilst approximating around 90% of E_J for the larger molecules, a proportion which increases with system extent.

We conclude our analysis of the KSJ approximation by studying a variety of biomolecules¹ and give these results in Table 4. In the $\omega = 0.4$ results we have found a clear correlation between the number and nature of the functional groups and the error in \tilde{E}_L . The azido group appears alone to lead to an error of around 2 millihartree (compare the error for N_2 in Table 2). Errors of around $0.4 m E_h$ 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 interaction error between well-separated aspherical nuclei is primarily dipolar and thus vanishes like R^{-3} . Despite this systematic error, the highly accurate treatment of the hydrocarbon backbone means that for all of the molecules in this table we are well within the Eichkorn criterion of $0.2 m E_h/\text{atom}$. These results suggest that the KSJ approximation is an excellent route to obtaining accurate Coulomb energies for medium to large biological systems.

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 $0.2 m E_h/\text{atom}$. 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 be computed extremely rapidly. Although we have not considered the optimization of the auxiliary basis set in this work, deferring this to future studies [26], we believe that quite compact basis sets will yield errors close to the Stewart limit. Combined with the efficient computation of E_S [29], the KWIK-Stewart approximation promises to be one of the most efficient 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 computations.

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¹ The geometries of these molecules are available on request.

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