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On an "interaction by moments" property of four center integrals.

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Abstract

The four center integrals needed in the Hartree Fock approximation and in TDDFT linear response are known to be difficult to calculate for orbitals of the Slater type or of finite range. We show that the interaction of pairs of products that do not mutually intersect may be replaced by the interaction of their moments, of which there are $O(N)$. Only quadruplets of orbitals 'close' to one another need an explicit calculation and the total calculational effort therefore scales as $O(N)$. We provide a new and concise proof of this "interaction by moments" property.

Motivation

This note is motivated by the occurrence of four center integrals in the TDDFT linear response equation [1], [2]

$$\chi = \frac{\delta\rho(r,t)}{\delta V_{ext}(r',t')} = \frac{1}{\chi_{KS}^{-1} - \left(\frac{\delta(t-t')}{|r-r'|} + \frac{\delta V_{xc}(r,t)}{\delta\rho(r',t')} \right)} \quad (1)$$

where $\chi_{KS} = \frac{\delta\rho}{\delta V_{KS}}$ and $\chi = \frac{\delta\rho}{\delta V_{ext}}$ are the free and interacting density response, where ρ denotes the electronic density and where V_{ext} is an external potential acting on the electrons. In a basis of local orbitals $\{f^a(r)\}$, the electronic density ρ and the external potential V_{ext} may be expanded in terms of products of such orbitals according to

$$\rho = \sum_{a,b} f^{a*} f^b \rho_{ab}, \quad V_{ext}^{ab} = \int dr V_{ext} f^{a*} f^b \quad (2)$$

Equation (1) then turns into a matrix equation for the response $\chi_{ab,cd} = \frac{\delta\rho_{ab}}{\delta V_{cd}}$ of $\rho_{ab}(t)$ with respect to variations of $V_{ext}^{cd}(t')$ and this equation then contains the Coulomb interaction between products of orbitals or 'four center integrals'

$$\langle 12 | \frac{1}{r} | 34 \rangle = \int dr dr' f^{1*}(r) f^2(r) \frac{1}{|r-r'|} f^{3*}(r') f^4(r') \quad (3)$$

A technique for calculating these quantities in terms of two center integrals was developed in [3]. In an alternative "resolution of identity" method, products of orbitals are replaced by auxiliary functions, see [4], [5].

For orbitals of finite range, there are, for N atoms, $O(N^2)$ pairs (12), (34) of individually intersecting orbitals suggesting the need of $O(N^2)$ distinct calculations. Here we show that only the subset of $\langle 12 | \frac{1}{r} | 34 \rangle$ where a pair (1,2) intersects with a pair (3,4) must be calculated explicitly, while the remaining ones can be taken into account by their multipolar interactions. Since there are only $O(N)$ such quadruplets of orbitals and because the effort of calculating the moments scales like N , the cost of calculating four center integrals then scales as $O(N)$.

The present note arose in an ongoing effort to implement linear response for extended molecular systems, an effort prompted by recent work [7]. We prove and exploit an observation of Greengard on the exact character of the "interaction by moments". This observation was rederived previously in the literature [6] and its consequence has recently been absorbed in a corresponding computer code [8], but our concise and simple deduction of this important property may still be of interest.

Reduction from four centers to two centers

We first need a reduction of products of orbitals to a set of single center functions. Following the discussion of [3] we obtain an expansion in spherical harmonics of a translated function $f(\vec{r} - \vec{a})$ by using its momentum representation

$$\begin{aligned} \psi_{lm}(\vec{r} - \vec{a}) &= \int \frac{d^3p}{(2\pi)^{3/2}} \psi_{lm}(\vec{p}) e^{-ip(r-a)} \\ \psi_{lm}(\vec{p}) &= i^l \tilde{\psi}_l(p) Y_{lm}(\vec{p}), \quad \tilde{\psi}_l(p) = \sqrt{\frac{2}{\pi}} \int_0^\infty r^2 \psi_l(r) j_l(pr) dr \end{aligned} \quad (4)$$

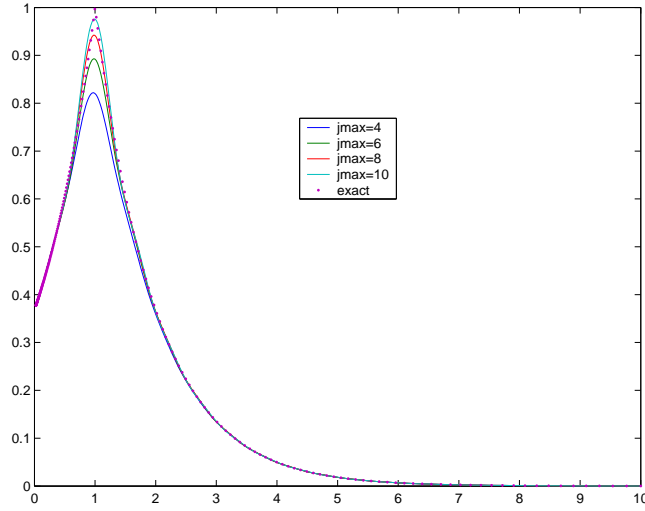


Figure 1: convergence towards a cusp with j_{\max}

We use spherical Bessel functions $j_l(x)$ with l integer, that are related to conventional Bessel functions for half integers by $j_l(x) = \sqrt{\frac{x}{2x}} J_{l+\frac{1}{2}}(x)$. In practice, fast Hankel transform routines [9] are needed to speed up the calculation. Expanding $e^{i\vec{p}\cdot\vec{r}}$ in spherical waves, one finds

$$\psi_{lm}(\vec{r} - \vec{a}) = \sum_{l_1 m_1} Y_{l_1 m_1}(\vec{r}) G_{l_1 m_1}(r) \quad (5)$$

where the coefficients $G_{l_1 m_1}(r)$ that multiply the spherical harmonics $Y_{l_1 m_1}(\vec{r})$ now depend on both quantum numbers l_1 and m_1 because spherical symmetry is lost. One has the following expression for $G_{l_1 m_1}(r)$

$$G_{l_1 m_1}(r) = 2\sqrt{8\pi} \sum_{l_2} F_{l_1 l_2}(r) Y_{l_2, m_1 - m}^*(\vec{a}) (-)^{l_1} (-)^{\frac{1}{2}(l_2 + l_1 + l)} G_{l_2, l_1 m_1 l_2 m_1 - m} \quad (6)$$

$$F_{l_1 l_2}(r) = \int_0^\infty j_{l_1}(pr) \tilde{\psi}_l(p) j_{l_2}(pa) p^2 dp$$

where $G_{l_1 m_1, l_2 m_2, l_3 m_3}$ are Gaunt coefficients for the overlap of three spherical harmonics. To bring this approach into perspective, it is interesting to consider an orbital with a cusp singularity such as e^{-r} and to study the convergence of the translated orbital towards a translated cusp with increasing angular momentum cutoff j_{\max} , see the figure. The figure shows that a fairly large number of angular harmonics is required for the representation of orbitals having such a cusp.

By applying translations to two overlapping orbitals we may obtain an expansion of their product about a common midpoint

$$\psi_{l_1 m_1}(\vec{r} - \vec{a}_1) \psi_{l_2 m_2}(\vec{r} - \vec{a}_2) = \sum_{l=0..l_{\max}, m=-l..l} G_{lm}(r) Y_{lm}(\vec{r}) \quad (7)$$

Using such expressions we can compute the Coulomb interaction of two pairs of mutually overlapping orbitals from the point of view of their associated effective centers.

Exact interaction by moments of non intersecting centers

We have seen that pairs of orbitals may be replaced by effective centers. Now we wish to show that the interaction between effective centers may be simplified when their spheres of support no longer intersect. We begin by quoting formulas for the computation of two center integrals in Fourier space, see [3], [10]

$$\langle 1 | \frac{1}{r} | 2 \rangle = \int \psi_{l_1 m_1}^*(r_1) \frac{1}{|r_1 - r_2|} \psi_{l_2 m_2}(r_2) d^3 r_1 d^3 r_2 = 4\pi \int \tilde{\psi}_{l_1 m_1}^*(\vec{p}) \frac{1}{p^2} \tilde{\psi}_{l_2 m_2}(\vec{p}) e^{i\vec{p}\cdot\vec{R}} d^3 p$$

where we used that $\frac{1}{|r_1 - r_2|} = -\frac{4\pi}{\Delta}$, Δ being the Laplace operator. Expanding $e^{i\vec{p}\cdot\vec{r}}$ in spherical waves one finds

$$\int \psi_{l_1 m_1}^*(r_1) \frac{1}{|r_1 - r_2|} \psi_{l_2 m_2}(r_2) d^3 r_1 d^3 r_2 = \sum_{lm} Y_{lm}(\vec{R}) C_{lm}^{l_1 m_1, l_2 m_2}(R) \quad (8)$$

with

$$\begin{aligned} C_{lm}^{l_1 m_1, l_2 m_2}(R) &= C_{l_1 l_2 l}(R) G_{l_1 m_1, l_2 m_2, lm} \\ C_{l_1 l_2 l}(R) &= (4\pi)^2 (-)^{\frac{1}{2}(l+l_2-l_1)} \int_0^\infty \tilde{\psi}_{l_1}^*(p) \tilde{\psi}_{l_2}(p) j_l(pR) dp \end{aligned} \quad (9)$$

where $G_{l_1 m_1, l_2 m_2, lm}$ are the previously encountered Gaunt coefficients and $C_{l_1 l_2 l}(R)$ are Wigner-Eckart like couplings, see [3], [10] for details of the derivation. We use eq(4) to rewrite the $C_{l_1, l_2, l}(R)$ in terms of the original radial wave functions as follows:

$$C_{l_1, l_2, l} = 32\pi (-)^{\frac{l+l_2-l_1}{2}} \int dr_1 dr_2 r_1^2 \tilde{\psi}_{l_1}^*(r_1) r_2^2 \tilde{\psi}_{l_2}(r_2) \int_0^\infty j_{l_1}(pr_1) j_{l_2}(pr_2) j_l(pR) dp \quad (10)$$

The "interaction by moments" property we are after is contained in the following integral of Bessel functions

$$I_{l_1, l_2, l}(r_1, r_2, R) = \int_0^\infty j_{l_1}(pr_1) j_{l_2}(pr_2) j_l(pR) dp \quad (11)$$

The Coulomb interaction coefficients $C_{l_1, l_2, l}$ would reduce to $I_{l_1, l_2, l}(r_1, r_2, R)$ if the original orbitals functions were concentrated at, respectively, radii r_1 and r_2 . This integral therefore represents the Coulomb interaction of two charged hollow shells of radii r_1, r_2 at a distance of R , and with the charge densities having the appropriate multipolar angular dependences. For $R > r_1 + r_2$ where these shells no longer intersect, we expect their interaction to simplify. Because of the Gaunt coefficients in eq(9) we only need this interaction for even values of $l_1 + l_2 + l$ and where a triangle inequality $|l_1 - l_2| \leq l \leq l_1 + l_2$ holds. In this case the integrand associated with the dp integration in eq(10) is symmetric as a function of p and we may therefore extend the domain of integration to the entire p axis:

$$I_{l_1, l_2, l}(r_1, r_2, R) = \frac{1}{2} \int_{-\infty}^\infty j_{l_1}(r_1 p) j_{l_2}(r_2 p) j_l(R p) dp \quad \text{for } l_1 + l_2 + l \text{ even}$$

It is convenient to use $j_l(z) = \text{Re } h_l(z)$ and to consider a corresponding complex integral $I_{l_1, l_2, l}^c$ with $I_{l_1, l_2, l} = \text{Re } I_{l_1, l_2, l}^c$ that involves the Hankel function $h_l(z)$:

$$I_{l_1, l_2, l}^c(r_1, r_2, R) = \frac{1}{2} \int_{-\infty}^\infty j_{l_1}(r_1 p) j_{l_2}(r_2 p) h_l(R p) dp, \quad (12)$$

For $R > r_1 + r_2$ the contour of integration in $I_{l_1, l_2, l}^c(r_1, r_2, R)$ can be closed at infinity in view of the relation

$$h_n(p) = (-)^n p^n \left(\frac{d}{p dp} \right)^n \frac{-i e^{ip}}{p} \quad (13)$$

Clearly, the exponential factor e^{iRp} from $j_l(Rp)$ dominates, for $R > r_1 + r_2$, the factors $e^{\pm i p r_1} e^{\pm i p r_2}$ that arise in the integrand in eq(12) from the product $j_{n_1}(r_1 p) j_{n_2}(r_2 p)$. Since the integrand in $I_{l_1, l_2, l}^c$ is analytic, except for possible singularities at $p = 0$ and since the contour of integration can be closed in the upper half plane, a non zero contribution to $I_{l_1, l_2, l}^c$ can only be due to a residue at $p = 0$. From eq(13) the most singular term in $h_l(Rp)$ at $p = 0$ is

$$h_l(Rp) = -i(2l-1)!! \frac{e^{iRp}}{(Rp)^{l+1}} + O(p^{-l})$$

Because of $j_{l_1}(r_1 p) \sim \frac{(r_1 p)^{l_1}}{(2l_1+1)!!}$ and an analogous relation for $j_{l_2}(r_2 p)$ a non zero residue is impossible in eq(12) unless l attains the maximal value permitted by the triangle inequality, $l = l_1 + l_2$. When setting $l = l_1 + l_2$ and closing the contour of integration in eq(12) at infinity, there is a term $\sim 1/p$ that provides a non zero result by elementary contour integration. Rewriting the result in terms of conventional Γ functions, one then finds, for $l = l_1 + l_2$ even and with $0 \leq l \leq l_1 + l_2$, the following simple result

$$I_{l_1, l_2, l}(r_1, r_2, R) = \delta_{l, l_1 + l_2} \frac{\pi^{3/2}}{8} \frac{r_1^{l_1} r_2^{l_2}}{R^{l+1}} \frac{\Gamma(l+1/2)}{\Gamma(l_2+3/2)\Gamma(l_1+3/2)} \quad (14)$$

Applied to the Coulomb interaction coefficients of eq(10) one concludes

$$\begin{aligned} C_{l_1, l_2, l} &= (-)^{\frac{l+l_2-l_1}{2}} \frac{\pi^{1/2}}{2^{l_1+l_2-l+2}} \frac{\rho_{l_1}^* \rho_{l_2}}{R^{l+1}} \frac{\Gamma(l+1/2)}{\Gamma(l_2+3/2)\Gamma(l_1+3/2)} \delta_{l, l_1 + l_2} \\ \rho_{l_1, 2} &= 4\pi \int_0^{r_1, 2} dr r^{2+l_1, 2} \tilde{\psi}_{l_1, 2}(r) \quad \text{for } R \geq r_1 + r_2 \end{aligned} \quad (15)$$

This last equation shows very clearly that non overlapping orbitals interact exactly via their moments, as shown first by Greengard [11]. For another proof, see [6].

Conclusion

We conclude that only the subset of four center integrals $< 12|\frac{1}{r}|34 >$ of "close" pairs where (1, 2) intersects (3, 4) must be calculated explicitly. Because there are only $O(N)$ such pairs of orbitals for a system of N atoms and because the multipoles are associated with only $O(N)$ products, the calculational effort scales as $O(N)$.

The conclusion that Coulomb integrals should be divided into far and near field ones has already been incorporated in a quantum chemistry code [8]. But our derivation of the "interaction by moments property" of four center integrals from a plain integral of a product of three spherical Bessel functions is the simplest and most concise proof of this property that is available.

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Figure caption: Translation away from the origin of e^{-r} by one unit, with $j \leq j_{\max} = 4, 6, 8, 10$ and the convergence of the result towards a cusp with increasing angular momentum cutoff j_{\max} .

References

- [1] M. Petersilka, U. J. Gossmann, and E. K. U. Gross, Phys. Rev. Lett. **76**, 1212-1215 (1996).
- [2] M. E. Casida, in "Recent Advances in Density Functional theory", edited by D.P. Chong, World Scientific, p.155 (1995)
- [3] J. D. Talman, J. Chem. Phys. **80**, 2000 (1984).
- [4] For a review, see K. Eichkorn, O. Treutler, H. Öhm, M. Häser and R. Ahlrichs, Chem. Phys. Lett. **240**, 283 (1995)
- [5] S.J.A.van Gisbergen, J.G.Snijders and E. J. Baerends, Comp. Phys. Comm 118 (1999) 119.
- [6] C.White and M. Head-Gordon, J. Chem. Phys. **101**, 6593 (1994).
- [7] X. Blase and P. Ordejón, Phys. Rev. **B 69**, 085111 (2004).
- [8] M. Sierka, A. Hogekamp, and R. Ahlrichs, J. Chem. Phys.**118**, 9136 (2003)
- [9] J.D. Talman, J. Comp. Phys., **29**, 35 (1978) and Comp.Phys. Comm. **30**, 93 (1983).
- [10] J. M. Soler, E.Artacho, J. D. Gale, A. García, J. Junquera, P. Ordejón and D. Sánchez-Portal J. Phys.**C 14**, 2745 (2002).
- [11] L. Greengard, "The rapid evaluation of potential fields in particle systems", Ph.D. thesis, Yale University, Cambridge, Mass., 1988.