Evaluation of Molecular Conditionally Convergent Integrals

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The problem of the evaluation of molecular integrals arising from electromagnetic interaction is well known [1, 2]. It is well documented [3, 4] that the true values of the divergent integrals are the principal part of them.

In this work we intend to describe a different procedure which is simpler and more direct than the ones previously introduced [1, 2]. The integrals to be evaluated are of the form:

$$\langle \psi_a | O_b | \psi_a \rangle = \int \psi_l(\boldsymbol{r}-\boldsymbol{a})\, \psi_n(\boldsymbol{r}-\boldsymbol{a})\, O_{ij}(\boldsymbol{r}-\boldsymbol{b})\, d\boldsymbol{r} \tag{1}$$

were ψ_l, ψ_n are Slater atomic orbitals centered on $\boldsymbol{a}$ and O_{ij} is the operator (electric field gradient) $\frac{\partial^2}{\partial i\,\partial j}\frac{1}{r}$ centered on $\boldsymbol{b}$ $(i, j = x, y, z)$.

First we evaluate the integral:

$$T = \int \varphi(\boldsymbol{a}-\boldsymbol{r})\, V(\boldsymbol{r}-\boldsymbol{b})\, \mathrm{d}\boldsymbol{r} \tag{2}$$

where $\varphi(\boldsymbol{r}) = \frac{1}{4\pi}\exp\{(-\alpha r)/r\}$ and $V(r) = 1/r$.

We evaluate the integral (2) by the substitution $\boldsymbol{r}\to\boldsymbol{r}+\boldsymbol{b}$ and by expanding the function $\varphi(\boldsymbol{R}-\boldsymbol{r})$ with $\boldsymbol{R}=\boldsymbol{a}-\boldsymbol{b}$ in a standard manner [5].

The contribution to the integral (2) by the volume εR is given with a function which has the value zero in the $\lim \varepsilon = 0$. The differentiation of this function is permisible because the derivatives are zero when $\varepsilon \to 0$. The behaviour of T thus allows the differentiation of the integral T with respect to parameters. The value of T is

$$T = \frac{1}{\alpha}\,\frac{1-e^{-X}}{X}, \quad X = \alpha R.$$

The integral (1) is calculated by finding the differential operator for the function under the integral sign and then operating with it on the integral (2)

If we use $2s(\psi_0)$ and $2p(\psi_l)$ A O the required expressions are

$$\psi_l(\boldsymbol{a}-\boldsymbol{r})\,\psi_n(\boldsymbol{a}-\boldsymbol{r}) = \zeta^3\alpha^2\left[\delta_{ln} - \frac{\partial^2}{\partial a_l\,\partial a_n}\frac{\partial}{\partial\alpha}\frac{1}{\alpha}\right]\frac{\partial}{\partial\alpha}\frac{1}{\alpha}\frac{\partial}{\partial\alpha}\varphi(\boldsymbol{a}-\boldsymbol{r})$$

$$\psi_0(\boldsymbol{a}-\boldsymbol{r})\,\psi_l(\boldsymbol{a}-\boldsymbol{r}) = \frac{\zeta^3\alpha^2}{\sqrt{3}}\frac{\partial}{\partial a_l}\frac{\partial^2}{\partial\alpha^2}\frac{1}{\alpha}\frac{\partial}{\partial\alpha}\varphi(\boldsymbol{a}-\boldsymbol{r})$$

$$\psi_0^2(\boldsymbol{a}-\boldsymbol{r}) = -\frac{\zeta^3\alpha^2}{3}\frac{\partial^3}{\partial\alpha^3}\varphi(\boldsymbol{a}-\boldsymbol{r})$$

with

$$l, n = 1\,(2p\,x),\ 2\,(2p\,y),\ 3\,(2p\,z);\ \alpha = 2\zeta;\ \boldsymbol{a} = (a_x, a_y, a_z)$$

$$V_{ij}(\boldsymbol{r}-\boldsymbol{b}) = \frac{\partial^2}{\partial i\,\partial j}\,(\boldsymbol{r}-\boldsymbol{b}) \qquad i, j = x, y, z$$

It is useful to define the elementary functions

$$p_k(X) = \sum_{j=0}^{\infty}(-1)^j\frac{X^j}{(j+k)\,j!} \qquad k \geqq 1$$

and to express the integral $T(X)$ as

$$T(X) = \frac{1}{\alpha}p_1(X), \quad p_1(X) = \frac{1-e^{-X}}{X}$$

The evaluation of the integral (1) can be done by using the elementary function p, and as an example the following integral is given [6] (m is the direction of $\boldsymbol{R}$)

$$T_{ii00}^{(m)} = \int \psi_0^2(\boldsymbol{a}-\boldsymbol{r})\, V_{ij}(\boldsymbol{r}-\boldsymbol{b})\,\mathrm{d}\boldsymbol{r}$$

$$T_{ij00}^{(m)} = \frac{1}{24R^3}X^3 e^{-X}[(\delta_{ij} - 3\,\delta_{im}\,\delta_{jm})\,(4+X) - \delta_{im}\,\delta_{jm}X^2 + 12\,(3\,\delta_{im}\,\delta_{jm} - \delta_{ij})\,e^X p_3(X)].$$

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[6] The values of all other integrals are available by request to M. Žaucer.