

Evaluation of Molecular Conditionally Convergent Integrals

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(Z. Naturforsch. 26 a, 326 [1971]; received 12 December 1970)

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:

$$\langle \psi_a | O_b | \psi_a \rangle = \int \psi_1(\mathbf{r}-\mathbf{a}) \psi_n(\mathbf{r}-\mathbf{a}) O_{ij}(\mathbf{r}-\mathbf{b}) d\mathbf{r} \quad (1)$$

where ψ_1, ψ_n are Slater atomic orbitals centered on \mathbf{a} and O_{ij} is the operator (electric field gradient) $\frac{\partial^2}{\partial i \partial j} \frac{1}{r}$ centered on \mathbf{b} ($i, j = x, y, z$).

First we evaluate the integral:

$$T = \int \varphi(\mathbf{a}-\mathbf{r}) V(\mathbf{r}-\mathbf{b}) d\mathbf{r} \quad (2)$$

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

We evaluate the integral (2) by the substitution $\mathbf{r} \rightarrow \mathbf{r} + \mathbf{b}$ and by expanding the function $\varphi(\mathbf{R}-\mathbf{r})$ with $\mathbf{R} = \mathbf{a} - \mathbf{b}$ in a standard manner⁵.

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 permissible because the derivatives are zero when $\varepsilon \rightarrow 0$. The behaviour of T thus allows the differentiation of the integral T with respect to parameters. The value of T is

Sonderdruckanforderungen an Dr. A. AŽMAN, Department of Chemistry, University of Ljubljana, Murnikova 6, P.O.B. 537, 61 001 Ljubljana, Jugoslawien.

¹ R. M. PITZER, C. W. KERN, and W. N. LIPSCOMB, J. Chem. Phys. **37**, 267 [1962].

² R. M. PITZER, J. Chem. Phys. **51**, 3191 [1969] and references therein.

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

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 $2p(\psi_1)$ AO the required expressions are

$$\begin{aligned} \psi_1(\mathbf{a}-\mathbf{r}) \psi_n(\mathbf{a}-\mathbf{r}) &= \zeta^3 \alpha^2 \left[\delta_{ln} - \frac{\partial^2}{\partial a_l \partial a_n} \frac{\partial}{\partial a} \frac{1}{\alpha} \right] \frac{\partial}{\partial \alpha} \frac{1}{\alpha} \frac{\partial}{\partial \alpha} \varphi(\mathbf{a}-\mathbf{r}) \\ \psi_0(\mathbf{a}-\mathbf{r}) \psi_1(\mathbf{a}-\mathbf{r}) &= \frac{\zeta^3 \alpha^2}{\sqrt{3}} \frac{\partial}{\partial a_l} \frac{\partial^2}{\partial a^2} \frac{1}{\alpha} \frac{\partial}{\partial \alpha} \varphi(\mathbf{a}-\mathbf{r}) \\ \psi_0^2(\mathbf{a}-\mathbf{r}) &= -\frac{\zeta^3 \alpha^2}{3} \frac{\partial^3}{\partial \alpha^3} \varphi(\mathbf{a}-\mathbf{r}) \end{aligned}$$

with

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

$$V_{ij}(\mathbf{r}-\mathbf{b}) = \frac{\partial^2}{\partial i \partial j} \frac{1}{r}(\mathbf{r}-\mathbf{b}) \quad i, j = x, y, z$$

It is useful to define the elementary functions

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

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 given⁶ (m is the direction of \mathbf{R})

$$\begin{aligned} T_{i00}^{(m)} &= \int \psi_0^2(\mathbf{a}-\mathbf{r}) V_{ij}(\mathbf{r}-\mathbf{b}) d\mathbf{r} \\ T_{ij00}^{(m)} &= \frac{1}{24 R^3} X^3 e^{-X} [(\delta_{ij} - 3\delta_{im}\delta_{jm})(4+X) - \\ &\quad - \delta_{im}\delta_{jm}X^2 + 12(3\delta_{im}\delta_{jm} - \delta_{ij})e^X p_3(X)]. \end{aligned}$$

³ H. A. BETHE and E. F. SALPETER, Quantum Mechanics of One- and Two Electron Atoms, Academic Press, Inc., New York 1957.

⁴ M. J. STEPHEN and J. P. AUFRAY, J. Chem. Phys. **31**, 1329 [1959].

⁵ P. M. MORSE and H. FESHBACH, Methods of Theoretical Physics, McGraw-Hill, Kogakusha 1953, p. 1574.

⁶ The values of all other integrals are available by request to M. ŽAUCER.