EVALUATION OF PSEUDOPOTENTIAL INTEGRALS OVER GAUSSIAN LOBE BASIS FUNCTIONS

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A mathematical analysis of molecular integrals of pseudopotential interactions in molecules is presented. The integrals are expressed over Gaussian lobe functions in the form suitable for computer programming.

The usefulness of the pseudopotential treatment in MO LCAO SCF calculations of molecules containing heavier atoms was discussed many-times elsewhere[1]. In the present paper we derived integrals for the three-parameter atomic pseudopotential which was proposed for the elements from lithium to krypton by Barthelat and co-workers[2]. If use is made of this pseudopotential, the following integrals arise:

$$I_1 = \langle \chi_I(\boldsymbol{r}_1) \mid r_{1C}^2 \exp(-\beta r_{1C}^2) \mid \chi_J(\boldsymbol{r}_1) \rangle \tag{1}$$

$$I_2 = \langle \chi_I(\boldsymbol{r}_1) \mid r_{1C}^{-1} \exp(-\beta r_{1C}^2) \mid \chi_J(\boldsymbol{r}_1) \rangle \tag{2}$$

$$I_3 = \langle \chi_I(\boldsymbol{r}_1) \mid r_{1C}^{-2} \exp(-\beta r_{1C}^2) \mid \chi_J(\boldsymbol{r}_1) \rangle , \tag{3}$$

where in place $\chi_I(\boldsymbol{r}_1)$ we will use the normalized Gaussian lobe function

$$\chi_I(\boldsymbol{r}_1) = N_I \exp(-\alpha_I r_{1I}^2) = N_I \exp\{-\alpha_I(\boldsymbol{r}_1 - \boldsymbol{r}_I)^2\} , \tag{4}$$

where $N_I = (2\alpha_I/\pi)^{3/4}$.
Considering the fact[3] that the product of two Gaussians yields again a Gaussian centered at

$$\boldsymbol{P} = (\alpha_I \boldsymbol{r}_I + \alpha_J \boldsymbol{r}_J)/(\alpha_I + \alpha_J) \tag{5}$$

we obtain

$$\chi_I(\boldsymbol{r}_1)\, \chi_J(\boldsymbol{r}_1) = \chi_P(\boldsymbol{r}_1) =$$

$$= N_I N_J \exp\{-\alpha_I \alpha_J r_{IJ}^2/(\alpha_I + \alpha_J)\} \exp\{-(\alpha_I + \alpha_J)\, r_{1P}^2\} , \tag{6}$$

where $\boldsymbol{r}_{1P} = \boldsymbol{r}_1 - \boldsymbol{r}_P$.

Because all the integrals (*1–3*) contain the exponential part from the pseudopotential we have

$$\chi_P(\mathbf{r}_1) \exp(-\beta r_{1C}^2) = \chi_Q(\mathbf{r}_1) = Z_{IJC} \exp(-\delta r_{1Q}^2) \tag{7}$$

and $\delta = \alpha_I + \alpha_J + \beta$

$$Z_{IJC} = N_I N_J \exp\{-\alpha_I \alpha_J r_{IJ}^2/(\alpha_I + \alpha_J)\} \exp\{-(\alpha_I + \alpha_J)\beta r_{PQ}^2/\delta\} \tag{8}$$

$$\mathbf{r}_Q = \{(\alpha_I + \alpha_J)\mathbf{r}_P + \beta \mathbf{r}_C\}/\delta .$$

These introductory expressions have been used in the derivation of the presented integrals.

Integral I_1

According to the above introduced mathematical simplifications this integral can be solved without any special transformation. We can write

$$I_1 = Z_{IJC} \int r_{1C}^2 \exp(-\delta r_{1Q}^2)\, d\mathbf{r}_{1Q} , \tag{9}$$

where $\mathbf{r}_{1C} = \mathbf{r}_1 - \mathbf{r}_C = \mathbf{r}_1 - \mathbf{r}_Q + (\mathbf{r}_Q - \mathbf{r}_C) = \mathbf{r}_{1Q} + \mathbf{r}_{CQ}$, and now

$$I_1 = Z_{IJC} \int_{-\infty}^{\infty} dx_{1Q} \int_{-\infty}^{\infty} dy_{1Q} \int_{-\infty}^{\infty} dz_{1Q} \,.$$

$$. \{(x_{1Q} + x_{CQ})^2 + (y_{1Q} + y_{CQ})^2 + (z_{1Q} + z_{CQ})^2\} \exp\{-\delta(x_{1Q}^2 + y_{1Q}^2 + z_{1Q}^2)\} , \tag{10}$$

and after simple integration

$$I_1 = Z_{IJC} (\pi/\delta)^{3/2} (3\delta/2 + r_{CQ}^2) . \tag{11}$$

Integral I_2

One can see that this integral leads to the nuclear attraction integral which can be solved using the following integral transformation

$$r_{1C}^{-1} = \frac{1}{2\pi^2} \int \frac{d\mathbf{k}}{k^2} \exp(i\mathbf{k} \,.\, \mathbf{r}_{1C}) . \tag{12}$$

The final formula was published in many papers[4,5], and according to our notation

$$I_2 = 2Z_{IJC}(\pi/\delta)\, F_0(\delta r_{CQ}^2) . \tag{13}$$

Here the function $F_0(y)$ is closely related to the error function

$$F_0(y) = \frac{1}{\sqrt{y}} \int_0^{\sqrt{y}} \exp(-\vartheta^2)\, \mathrm{d}\vartheta = \tfrac{1}{2}\sqrt{(\pi/y)}\, \mathrm{erfc}(\sqrt{y})\,. \tag{14}$$

Integral I_3

The formula for the last integral we derived using the following general transformation[3]

$$r^{-\lambda} = 1/\Gamma(\lambda/2) \int_0^{\infty} \mathrm{d}\alpha\, \alpha^{\lambda/2-1} \exp(-\alpha r^2)\,, \quad (\lambda, r > 0)\,. \tag{15}$$

In our case for $\lambda = 2$ (note that $\Gamma(1) = 1$)

$$r_{1C}^{-2} = \int_0^{\infty} \mathrm{d}\alpha \exp(-\alpha r_{1C}^2)\,, \tag{16}$$

after application of the integral transformation (*16*) integral I_3 becomes

$$I_3 = Z_{1JC} \int_0^{\infty} \mathrm{d}\alpha \exp(-\alpha r_{CQ}^2) \int \mathrm{d}r_{1Q} \exp\{-(\alpha + \delta)\, r_{1Q}^2 - 2\alpha \mathbf{r}_{CQ} \,.\, \mathbf{r}_{1Q}\} \tag{17}$$

or in the component form

$$\begin{aligned} I_3 = Z_{1JC} \int_0^{\infty} \mathrm{d}\alpha \exp(-\alpha r_{CQ}^2) \int_{-\infty}^{\infty} \mathrm{d}x_{1Q} \int_{-\infty}^{\infty} \mathrm{d}y_{1Q} \int_{-\infty}^{\infty} \mathrm{d}z_{1Q}\,. \\ .\, \exp\{-(\alpha + \delta)\, x_{1Q}^2 - 2\alpha x_{CQ} x_{1Q}\} \exp\{-(\alpha + \delta)\, y_{1Q}^2 - \\ - 2y_{CQ} y_{1Q}\} \exp\{-(\alpha + \delta)\, z_{1Q}^2 - 2z_{CQ} z_{1Q}\}\,. \end{aligned} \tag{18}$$

After substitution

$$a_\nu = \nu_{1Q} + (\alpha + \delta)\, \nu_{CQ}/\alpha\,, \quad (\nu = x, y, z) \tag{19}$$

we find

$$I_3 = Z_{1JC}\, \pi^{3/2} \int_0^{\infty} \mathrm{d}\alpha (\alpha + \delta)^{-3/2} \exp\left(-\frac{\alpha}{\alpha/\delta + 1}\, r_{CQ}^2\right). \tag{20}$$

Introducing

$$\alpha/\delta + 1 = 1/q \tag{21}$$

we obtain

$$I_3 = Z_{\mathrm{UC}}\pi^{3/2}|r_{\mathrm{CQ}}| \exp(\delta r_{\mathrm{CQ}}^2)\, \delta^{-1/2} \int_0^1 q^{-1/2} \exp(-\delta q r_{\mathrm{CQ}}^2)\, \mathrm{d}q\,, \qquad (22)$$

and finally after simple integration

$$I_3 = Z_{\mathrm{UC}}\pi^2\delta^{-1/2} \exp[(\delta r_{\mathrm{CQ}}^2)\, \mathrm{erfc}\, \sqrt{(\delta r_{\mathrm{CQ}}^2)}]\,. \qquad (23)$$

CONCLUSIONS

The present formulae are simpler than those in ref.[2] and they avoid the numerical integration. The formulae have been implanted in our LCAO MO SCF program based on the Gaussian lobe functions, and on the obtained results will be reported later.

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