

Two—Electron, One— and Two—Center Integrals

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PMDA/THF to the dissociated radical ions. Another observation consistent with the above results is that solutions of nitrobenzene in mesitylene yield photo-induced ESR signals, whereas solutions of TCNE do not. Hydrogen abstraction by the nitro compound in mesitylene apparently takes place readily under the influence of the mercury arc, whereas electron transfer from the π system of mesitylene to TCNE is much more difficult. In THF both α -hydrogen abstraction and electron transfer from the oxygen's nonbonding electrons can take place. Finally, the ESR spectrum observed for the TCNE/THF system is in good agreement with that of TCNE $^-$ prepared by standard methods. There is no indication of a further splitting by a proton, nor is the spectrum perturbed in any noticeable manner.

No evidence for a positive free radical ion has been obtained. If THF positive ion were present its steady-state concentration must be quite small. We believe, however, that THF positive ion is an unstable intermediate and quickly dimerizes or disproportionates to a diamagnetic product.

We have suggested that the incident light from the mercury arc produced an electron transfer from the donor molecule, THF, to the acceptor molecule, TCNE, followed by a dissociation of the complex. It is known that TCNE forms 1:1 charge transfer complexes with THF, tetrahydropyran, and *p*-dioxane. The absorption bands are broad and structureless with maxima at 318, 330, and 350 $m\mu$, respectively.⁶ Although we have found no data about charge transfer complexes of PMDA and ethers, it is known that the maximum of the absorption bands for PMDA and common donors appears in the region 330–385 $m\mu$.⁷ We have observed, with appropriate Bausch & Lomb narrow band pass filters, that the region of absorption required for the photoproduction of TCNE anion agrees with the charge transfer absorption maxima of 318 $m\mu$. This same wavelength region produces PMDA negative ion. It thus appears that the charge transfer complexes between TCNE and THF and between PMDA and THF are intimately connected with the photoproduction of TCNE $^-$ and PMDA $^-$.

TCNE $^-$ in tetrahydropyran has also been produced by continuous light irradiation through a narrow band pass filter which had $\sim 14\%$ transmission at 330 $m\mu$ and a full width at half maximum of 20 $m\mu$. Although no signal has been observed from solutions of TCNE in *p*-dioxane, signals have been obtained from solutions of TCNE in α -methyltetrahydrofuran and *N,N*-Dimethylformamide. It is noteworthy that ESR signals from TCNE/THF could be observed from solutions which had been subjected only to "room light." It was necessary to perform "dark experiments" to prevent an initial ESR signal. Also, in high concentration, $\sim 0.1M$ TCNE, the photoproduced TCNE $^-$ is quite stable and will exist for hours after the light is extinguished.

* Work performed under the auspices of the U.S. Atomic Energy Commission.

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Two-Electron, One- and Two-Center Integrals

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IN a recent note,¹ Prosser and Blanchard mentioned the use of the Fourier convolution theorem method for the evaluation of one-electron, two-center integrals. This method has been applied by the author to one-electron integrals involving nonintegral Slater orbitals² and to one-electron integrals involving solid spherical harmonic operators.³

The present note is concerned with the application of this method to the evaluation of two-electron, two-center integrals⁴ (see Fig. 1) of the type

$$I = \int f(\mathbf{r}_{a1}) g(\mathbf{r}_{b2}) h(\mathbf{r}_{12}) d\mathbf{r}_1 d\mathbf{r}_2. \quad (1)$$

The integral is recovered by

$$I = (2\pi)^{-3} \int \bar{f}(\mathbf{k}) \bar{g}(\mathbf{k}) \bar{h}(\mathbf{k}) \exp(-i\mathbf{k} \cdot \mathbf{R}) d\mathbf{k}, \quad (2)$$

where the bar indicates the appropriate Fourier transform

$$\bar{\phi}(\mathbf{k}) = \int \exp(i\mathbf{k} \cdot \mathbf{r}) \phi(\mathbf{r}) d\mathbf{r}. \quad (3)$$

In the corresponding one-center case (the limit as \mathbf{R} goes to zero), the centers *a* and *b* coalesce (so that

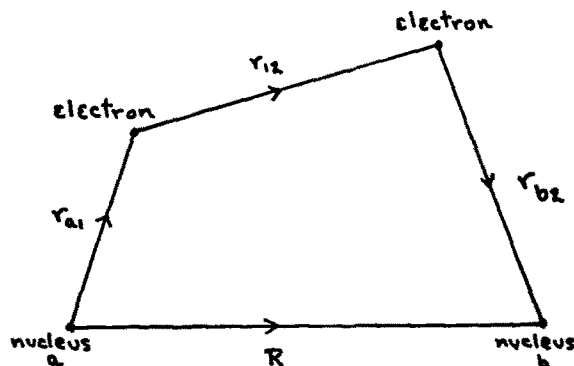


FIG. 1. Coordinate system.

the subscripts a and b can be dropped) giving rise to the integral

$$J = \int f(\mathbf{r}_1) g(\mathbf{r}_2) h(\mathbf{r}_{12}) d\mathbf{r}_1 d\mathbf{r}_2, \quad (4)$$

which is recovered by

$$J = (2\pi)^{-3} \int \tilde{f}(\mathbf{k}) \tilde{g}(\mathbf{k}) \tilde{h}(\mathbf{k}) d\mathbf{k}. \quad (5)$$

As an example of Eqs. (4) and (5), Pitzer and Hameka⁵ have discussed the one-center integral

$$J = (32\pi)^{-2} \int r_1^4 \cos^2\theta_1 r_2^4 \cos^2\theta_2 (r_{12}^{-3} - 3z_{12}^2 r_{12}^{-5}) \\ \times \exp(-r_1 - r_2) \sin\theta_1 \sin\theta_2 dr_1 dr_2 d\theta_1 d\theta_2 d\phi_1 d\phi_2. \quad (6)$$

The transform⁶ of $f(\mathbf{r}_1) = r_1^2 \cos^2\theta_1 \exp(-r_1)$ is given by

$$\tilde{f}(\mathbf{k}) = 32\pi(1+k^2)^{-4} [1 - k^2 - 4k^2 P_2(\cos u)]. \quad (7)$$

Since the function $g(\mathbf{r}_2)$ is identical, its transform is also given by Eq. (7). For the transform of

$$h(\mathbf{r}_{12}) = r_{12}^{-3} - 3z_{12}^2 r_{12}^{-5} = -2P_2(\cos\theta_{12})/r_{12}^3, \quad (8)$$

we have

$$\tilde{h}(\mathbf{k}) = 8\pi P_2(\cos u)/3. \quad (9)$$

After substituting Eqs. (7) and (9) into Eq. (5), and integrating over u and v (the angular components of the \mathbf{k} vector), we find

$$J = \frac{32\pi}{105} \left[11 \int_0^\infty \frac{k^6}{(1+k^2)^8} dk - 7 \int_0^\infty \frac{k^4}{(1+k^2)^8} dk \right]. \quad (10)$$

When these two simple integrals of Eq. (10) are evaluated, the result $J = -\frac{1}{1680}$ is obtained in agreement with the result quoted by Pitzer and Hameka.⁵

An interesting point to notice is that this method does not involve the introduction of delta-function terms. The method is further not limited to one-center nor to specific forms for the f , g , and h functions.

The author wishes to acknowledge the informative discussions with Dr. Howard B. Levine of North American Aviation Science Center as to the range of validity of the Fourier convolution theorem.

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⁶ See Ref. 3 for the method of evaluation of the transforms in detail.