Analytical Evaluation of Multicenter Integrals of r_{12}^{-1} with Slater-Type Atomic Orbitals IV. Four-Center Integrals by Taylor Series Method*

KENNETH G. KAY† AND HARRIS J. SILVERSTONE
Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218
(Received 23 December 1968)

The four-center integral of r_{12}^{-1} with Slater-type atomic orbitals is evaluated analytically. The result, obtained after expanding r_{12}^{-1} in a Taylor series, is for general values of the n, l, m, and ζ parameters of the Slater-type orbitals and of the internuclear distance vectors, $\mathbf{\mathcal{R}}_1$, $\mathbf{\mathcal{R}}_2$, and $\mathbf{R}$.

INTRODUCTION

Analytical formulas are derived for the four-center integral of r_{12}^{-1} with Slater-type atomic orbitals. The formulas are valid for general values of the quantum numbers, orbital exponents, and internuclear distances and angles. The basic techniques used in this paper are contour integration and the Taylor series expansion of r_{12}^{-1}.

This paper represents a departure from the Fourier-transform convolution theorem approach of Papers I–III,[1–3] an approach we shall return to in a subsequent paper.[4] The r_{12}^{-1} Taylor series approach (which is closely related to the bipolar expansion method[5a]) has been developed principally by Roberts, who obtained the four-center integral as an infinite sum of one-dimensional integrals,[5b] whose integrands in turn were products of two-center overlap integrals. Roberts advocated[5b] evaluating these one-dimensional integrals numerically. We resolve the one-dimensional integrals analytically, and the results are somewhat easier to obtain than (although somewhat different from) the results we have obtained[4] with the Fourier-transform convolution method. However, it is not certain which method yields the more useful result, because the Taylor-series approach contains more infinite summations.

FORMULATION IN TERMS OF OVERLAP INTEGRALS

Consider the four-center integral

$$I_{n_cl_cm_c\zeta_c,n_dl_dm_d\zeta_d;n_al_am_a\zeta_a,n_bl_bm_b\zeta_b}(\mathcal{R}_1,\mathcal{R}_2,\mathbf{R})\equiv(N_aN_bN_cN_d)^{-1}\int dV_1\int dV_2r_{12}^{-1}$$
$$\times[\psi^*_{n_cl_cm_c\zeta_c}(\mathbf{r}_2)\psi_{n_dl_dm_d\zeta_d}(\mathbf{r}_2-\mathcal{R}_2)]^*[\psi^*_{n_al_am_a\zeta_a}(\mathbf{r}_1-\mathbf{R})\psi_{n_bl_bm_b\zeta_b}(\mathbf{r}_1-\mathbf{R}-\mathcal{R}_1)] \quad (1)$$
$$=I_{cd;ab}(\mathcal{R}_1,\mathcal{R}_2,\mathbf{R}), \quad (2)$$

where the Slater-type orbitals are defined by

$$\psi_{nlm\zeta}(\mathbf{r})\equiv Nr^{n-1}\exp(-\zeta r)Y_l^m(\theta,\phi). \quad (3)$$

The n and l are positive integers which satisfy

$$n\geq l+1, \quad (4)$$

and the Y_l^m is a spherical harmonic.

Following Roberts,[5b] we obtain $I_{cd;ab}$ as a sum of Laplace transforms of products of two-center overlap intergals. Define

$$\boldsymbol{\rho}_1=\mathbf{r}_1-\mathbf{R}. \quad (5)$$

Then[5b]

$$r_{12}^{-1}=|\boldsymbol{\rho}_1+\mathbf{R}-\mathbf{r}_2| \quad (6)$$
$$=\sum_{i=0}^{\infty}\sum_{j=0}^{\infty}\sum_{k=0}^{\infty}\sum_{l=0}^{i+k}\sum_{m=-l}^{l}\sum_{L=0}^{j+k}\sum_{M=-L}^{L}c(l,m,L,M;k,j,i;\mathbf{R})Y_l^m(\theta_{\rho 1},\phi_{\rho 1})Y_L^M(\theta_2,\phi_2)$$
$$\times[i!j!k!(2i+2j+2k)!!]^{-1}\rho_1^{i+k}r_2^{j+k}\left(-\frac{d}{dR}\right)^{2i+2j+2k}\int_0^{\infty}du\exp[-(\rho_1+r_2+R)u], \quad (7)$$

* Supported in part by a National Science Foundation Grant.
† National Aeronautics and Space Administration Predoctoral Trainee.
1 H. J. Silverstone, J. Chem. Phys. **48,** 4098 (1968), hereafter referred to as I.
2 H. J. Silverstone, J. Chem. Phys. **48,** 4106 (1968), hereafter referred to as II.
3 H. J. Silverstone and K. G. Kay, J. Chem. Phys. **48,** 4108 (1968), hereafter referred to as III.
4 H. J. Silverstone and K. G. Kay (to be published).
5 (a) See, for instance: B. C. Carlson and G. S. Rushbrooke, Proc. Cambridge Phil. Soc. **46,** 626 (1950); R. J. Buehler and J. O. Hirschfelder, Phys. Rev. **83,** 628 (1951); **85,** 149 (1952); and R. A. Sack, J. Math. Phys. **5,** 260 (1964); (b) P. J. Roberts, J. Chem. Phys. **47,** 2981 (1967).

where

$$(2N)!!=2^N N!, \tag{8}$$

$$(2N-1)!!=(2N)!/(2N)!!, \tag{9}$$

and where $c(lm, LM; kji; \mathbf{R})$, which is given by Roberts,[6] is

$$c(lm, LM; kji; \mathbf{R})=R^{i+j}(4\pi)^2(-1)^M \sum_{l_1=0}^{k} \sum_{l_2=|L-l_1|}^{\min(j,L+l_1)} \sum_{l_3=|l-l_1|}^{\min(i,l+l_1)} \sum_{m_1=-l_1}^{l_1}$$

$$\times \frac{2^{i+j+k}(i!j!k!)^2(-1)^{l_3}[(2l_2+1)(2l_3+1)]^{1/2}}{(k-l_1)!(k+l_1+1)!(j-l_2)!(j+l_2+1)!(i-l_3)!(i+l_3+1)!}$$

$$\times c^{l_2}(L, -M; l_1m_1)c^{l_3}(lm; l_1m_1)Y_{l_2}{}^{-M-m_1}(\theta_R, \phi_R)Y_{l_3}{}^{m-m_1*}(\theta_R, \phi_R). \tag{10}$$

The (R, θ_R, ϕ_R), etc., denote the spherical coordinates of $\mathbf{R}$, etc. With Eq. (7) substituted into Eq. (1), and with the use of the Condon–Shortley coefficients,[7]

$$c^{\Lambda_1}(l_am_a; lm)\equiv\left(\frac{4\pi}{2\Lambda_1+1}\right)^{1/2}\int d\Omega Y_l{}^m Y_{\Lambda_1}{}^{m_a-m}Y_{l_a}{}^{m_a*}, \tag{11}$$

the $I_{cd;ab}$ becomes

$$I_{cd;ab}=\sum_{ijk}\sum_{lmLM}\sum_{\Lambda_1=|l-l_a|}^{l+l_a}\sum_{\Lambda_2=|L-l_c|}^{L+l_c} c(lm, LM; kji; \mathbf{R})[i!j!k!(2i+2j+2k)!!4\pi]^{-1}$$

$$\times[(2\Lambda_1+1)(2\Lambda_2+1)]^{1/2}c^{\Lambda_1}(l_am_a; lm)c^{\Lambda_2}(l_cm_c; L, -M)(-1)^M\left(-\frac{d}{dR}\right)^{2i+2j+2k} I'_{cd;ab}, \tag{12}$$

where

$$I'_{cd;ab}=\int_0^\infty du\,\exp(-Ru)\,S_{n_a+i+k,\Lambda_1,m_a-m,\zeta_a+u;n_bl_bm_b\zeta_b}(\mathfrak{R}_1)\,S^*_{n_c+j+k,\Lambda_2,m_c+M,\zeta_c+u;n_dl_dm_d\zeta_d}(\mathfrak{R}_2), \tag{13}$$

and where the S denotes the overlap integral

$$S_{n_1l_1m_1\zeta_1;n_2l_2m_2\zeta_2}(\mathfrak{R})\equiv(N_1N_2)^{-1}\int dV\psi^*_{n_1l_1m_1\zeta_1}(\mathbf{r})\psi_{n_2l_2m_2\zeta_2}(\mathbf{r}-\mathfrak{R}). \tag{14}$$

Equations (12) and (13) are essentially the results of Roberts.[5]

EVALUATION

To resolve $I'_{cd;ab}$ [Eq. (13)] we first use a convenient expression for the overlap integral[8]:

$$S_{n_1l_1m_1\zeta_1;n_2l_2m_2\zeta_2}(\mathfrak{R})=(-1)^{l_1+1}\pi^{1/2}\left(-\frac{d}{d\zeta_1}\right)^{n_1-l_1}\left(-\frac{d}{d\zeta_2}\right)^{n_2-l_2}\sum_{\lambda=|l_1-l_2|}^{l_1+l_2}(2\lambda+1)^{1/2}c^\lambda(l_2m_2; l_1m_1)Y_\lambda{}^{m_2-m_1}(\theta_\mathfrak{R}, \phi_\mathfrak{R})$$

$$\times\Bigg[(-1)^{l_2}\left(\zeta_1^{-1}\frac{d}{d\zeta_1}\right)^{l_1}\zeta_1{}^{l_1+l_2+1}\mathcal{K}_\lambda(\zeta_1\mathfrak{R})\left(\zeta_1^{-1}\frac{d}{d\zeta_1}\right)^{l_2}\zeta_1{}^{-1}[(\zeta_2+\zeta_1)^{-1}-(\zeta_2-\zeta_1)^{-1}]$$

$$+(-1)^{l_1}\left(\zeta_2^{-1}\frac{d}{d\zeta_2}\right)^{l_2}\zeta_2{}^{l_1+l_2+1}\mathcal{K}_\lambda(\zeta_2\mathfrak{R})\left(\zeta_2^{-1}\frac{d}{d\zeta_2}\right)^{l_1}\zeta_2{}^{-1}[(\zeta_1+\zeta_2)^{-1}-(\zeta_1-\zeta_2)^{-1}]\Bigg]. \tag{15}$$

The $\mathcal{K}_\lambda$ function is[9]

$$\mathcal{K}_\lambda(y)=(-y)^\lambda(y^{-1}d/dy)^\lambda y^{-1}\exp(-y). \tag{16}$$

---

[6] See Appendix of Ref. 5(b).

[7] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, London, 1935).

[8] H. J. Silverstone, J. Chem. Phys. **45**, 4337 (1966). Equation (15) above is a more concise form of Eq. (32) of this reference. This formula is an essential contribution of the Fourier-transform convolution method to the Taylor series method.

[9] The $\mathcal{K}_\lambda$ is essentially a modified spherical Bessel function of the third kind [see, e.g., M. Abramowitz and I. A. Stegun (Eds.), Natl. Bur. Std. (U.S.) Appl. Math. Ser. No. 55 (1964)]. The exponential-type integrals $E_n(x)$ are also discussed in this reference. Note that $\tilde{E}_1(x)$ is

$$\tilde{E}_1(x)=-\sum_{n=1}^{\infty}\frac{(-x)^n}{[nn!]}.$$

Some properties of the $\mathcal{K}_\lambda$, E_n, and $\tilde{E}_n$ functions are discussed in I. See especially Eqs. (16), (21)–(29), and (62)–(65). Note that the left-hand side of Eq. (21) of I should read $\tilde{E}_n(x)$. Unfortunately, the "∼" seems to have broken off during the printing.

Equation (15), put into Eq. (13), gives

$$I'_{cd;ab}=(-1)^{\Lambda_1+\Lambda_2}\pi\left(-\frac{d}{d\zeta_a}\right)^{n_a+i+k-\Lambda_1}\left(-\frac{d}{d\zeta_b}\right)^{n_b-l_b}\left(-\frac{d}{d\zeta_c}\right)^{n_c+j+k-\Lambda_2}\left(-\frac{d}{d\zeta_d}\right)^{n_d-l_d}$$

$$\times\sum_{\lambda_1=|\Lambda_1-l_b|}^{\Lambda_1+l_b}\sum_{\lambda_2=|\Lambda_2-l_d|}^{\Lambda_2+l_d}[(2\lambda_1+1)(2\lambda_2+1)]^{1/2}c^{\lambda_1}(l_bm_b;\Lambda_1,m_a-m)c^{\lambda_2}(l_dm_d;\Lambda_2,m_c+M)$$

$$\times Y_{\lambda_1}{}^{m_b-m_a+m}(\theta_{\mathcal{R}_1},\phi_{\mathcal{R}_1})Y_{\lambda_2}{}^{m_d-m_c-M*}(\theta_{\mathcal{R}_2},\phi_{\mathcal{R}_2})I''_{cd;ab},\quad(17)$$

with

$$I''_{cd;ab}=\int_0^\infty du\exp(-Ru)\left[(-1)^{l_b}\left((\zeta_a+u)^{-1}\frac{d}{du}\right)^{\Lambda_1}(\zeta_a+u)^{\Lambda_1+l_b+1}\mathcal{K}_{\lambda_1}[(\zeta_a+u)\mathcal{R}_1]\left((\zeta_a+u)^{-1}\frac{d}{du}\right)^{l_b}(\zeta_a+u)^{-1}\right.$$

$$\times[(\zeta_b+\zeta_a+u)^{-1}-(\zeta_b-\zeta_a-u)^{-1}]+(-1)^{\Lambda_1}\left(\zeta_b^{-1}\frac{d}{d\zeta_b}\right)^{l_b}\zeta_b^{\Lambda_1+l_b+1}\mathcal{K}_{\lambda_1}(\zeta_b\mathcal{R}_1)\left(\zeta_b^{-1}\frac{d}{d\zeta_b}\right)^{\Lambda_1}\zeta_b^{-1}$$

$$\left.\times[(\zeta_a+u+\zeta_b)^{-1}-(\zeta_a+u-\zeta_b)^{-1}]\right]\left[(-1)^{l_d}\left((\zeta_c+u)^{-1}\frac{d}{du}\right)^{\Lambda_2}(\zeta_c+u)^{\Lambda_2+l_d+1}\mathcal{K}_{\lambda_2}[(\zeta_c+u)\mathcal{R}_2]\right.$$

$$\times\left((\zeta_c+u)^{-1}\frac{d}{du}\right)^{l_d}(\zeta_c+u)^{-1}[(\zeta_d+\zeta_c+u)^{-1}-(\zeta_d-\zeta_c-u)^{-1}]+(-1)^{\Lambda_2}\left(\zeta_d^{-1}\frac{d}{d\zeta_d}\right)^{l_d}\zeta_d^{\Lambda_2+l_d+1}$$

$$\left.\times\mathcal{K}_{\lambda_2}(\zeta_d\mathcal{R}_2)\left(\zeta_d^{-1}\frac{d}{d\zeta_d}\right)^{\Lambda_2}\zeta_d^{-1}[(\zeta_c+u+\zeta_d)^{-1}-(\zeta_c+u-\zeta_d)^{-1}]\right].\quad(18)$$

Equation (18) can be resolved by contour integration techniques and the residue theorem. First turn the integral (18) into a contour integral by the manipulation

$$\int_0^\infty du\exp(-Ru)\cdots=(2\pi i)^{-1}\int_{\infty\exp(i\epsilon)}^{(0+)}du\log(-u)\exp(-Ru)\cdots.\quad(19)$$

[For convenience, we have shifted the integration path to the ray, $\arg(z)=\epsilon$, where ϵ is a small positive number.] With Eq. (19), $I''_{cd;ab}$ [Eq. (18)] breaks naturally into four terms,

$$I''_{cd;ab}=I^{(1)}+I^{(2)}+I^{(3)}+I^{(4)}.\quad(20)$$

We discuss $I^{(1)}$, the most difficult term, in detail, and then give results for the rest.

$I^{(1)}$ is defined by

$$I^{(1)}\equiv(-1)^{l_b+l_d}(2\pi i)^{-1}\int_{\infty\exp(i\epsilon)}^{(0+)}du\log(-u)\exp(-Ru)\{\Lambda_1\mid\mathcal{K}_{\lambda_1}[(\zeta_a+u)\mathcal{R}_1]\mid l_b\}$$

$$\times[(\zeta_a+\zeta_b+u)^{-1}-(\zeta_b-\zeta_a-u)^{-1}]\{\Lambda_2\mid\mathcal{K}_{\lambda_2}[(\zeta_c+u)\mathcal{R}_2]\mid l_d\}[(\zeta_c+\zeta_d+u)^{-1}-(\zeta_d-\zeta_c-u)^{-1}]\quad(21)$$

where we have defined

$$\{\Lambda\mid\mathcal{K}_\lambda(\zeta\mathcal{R})\mid l\}\equiv(\zeta^{-1}d/d\zeta)^\Lambda\zeta^{l+\Lambda+1}\mathcal{K}_\lambda(\zeta\mathcal{R})(\zeta^{-1}d/d\zeta)^l\zeta^{-1}\quad(22)$$

to save space.

After suitable manipulation, $I^{(1)}$ can be evaluated as a sum of residues. First note that since

$$\mathcal{K}_\lambda(y)\sim y^{-1}\exp(-y),\quad\text{as}\quad y\rightarrow\infty,\quad(23)$$

the integrand behaves like

$$\log(-u)\exp[-(R+\mathcal{R}_1+\mathcal{R}_2)u]u^{-l_b-l_d-4}\quad(24)$$

as $u\rightarrow\infty$. Second, note that the only singularities of the integrand of (22), besides the logarithm, are poles[10] at $u=-\zeta_a\pm\zeta_b$ and $-\zeta_c\pm\zeta_d$. Third, use the maneuver

$$\log(-u)=\tilde{E}_1[-u(R+\mathcal{R}_1+\mathcal{R}_2)]-E_1[-u(R+\mathcal{R}_1+\mathcal{R}_2)]-\log(R+\mathcal{R}_1+\mathcal{R}_2)-\gamma,\quad(25)$$

[10] What look like possible poles at $u=-\zeta_a$ and $-\zeta_c$ are not really there. See below, Eq. (34), and accompanying discussion.

where $E_1(x)$[9] is an exponential-type integral,

$$E_1(x)=\int_1^\infty dt t^{-1}\exp(-xt), \tag{26}$$

$$\sim x^{-1}\exp(-x),\quad \text{as}\quad x\rightarrow\infty, \tag{27}$$

the γ is Euler's constant, and $\tilde{E}_1(x)$ is an entire function.[9] Because the contour in Eq. (21) encloses no singularities other than $\log(-u)$, when Eq. (25) is put into Eq. (21), the contributions of $\tilde{E}_1$, $\log(R+\mathcal{R}_1+\mathcal{R}_2)$, and γ vanish. Because of Eqs. (27) and (24), the integrand of the term involving E_1 goes like $u^{-l_b-l_d-5}$, for large $|u|$, and the contour can be closed at ∞ by a circle running clockwise from $[\infty\exp(i\epsilon)-i\epsilon]$ to $[\infty\exp(i\epsilon)+i\epsilon]$. The integration path now surrounds four poles and no branch points, and the integral is immediately evaluated via the residue theorem:

$$\begin{aligned}I^{(1)}=(-1)^{l_b+l_d}\big((-1)^{\lambda_1}&\{l_b\mid \mathcal{K}_{\lambda_1}(-\zeta_b\mathcal{R}_1)\mid \Lambda_1\}\exp[(\zeta_a+\zeta_b)R]E_1[(\zeta_a+\zeta_b)(R+\mathcal{R}_1+\mathcal{R}_2)]\\
&\times\{\Lambda_2\mid \mathcal{K}_{\lambda_2}[(-\zeta_a-\zeta_b+\zeta_c)\mathcal{R}_2]\mid l_d\}[(-\zeta_a-\zeta_b+\zeta_c+\zeta_d)^{-1}-(\zeta_a+\zeta_b-\zeta_c+\zeta_d)^{-1}]+(-1)^{\lambda_1}\{l_b\mid \mathcal{K}_{\lambda_1}(\zeta_b\mathcal{R}_1)\mid\Lambda_1\}\\
&\times\exp[(\zeta_a-\zeta_b)R]E_1[(\zeta_a-\zeta_b)(R+\mathcal{R}_1+\mathcal{R}_2)]\{\Lambda_2\mid \mathcal{K}_{\lambda_2}[(-\zeta_a+\zeta_b+\zeta_c)\mathcal{R}_2]\mid l_d\}[(-\zeta_a+\zeta_b+\zeta_c+\zeta_d)^{-1}\\
&-(\zeta_a-\zeta_b-\zeta_c+\zeta_d)^{-1}]+(-1)^{\lambda_2}\{l_d\mid \mathcal{K}_{\lambda_2}(-\zeta_d\mathcal{R}_2)\mid\Lambda_2\}\exp[(\zeta_c+\zeta_d)R]E_1[(\zeta_c+\zeta_d)(R+\mathcal{R}_1+\mathcal{R}_2)]\\
&\times\{\Lambda_1\mid \mathcal{K}_{\lambda_1}[(\zeta_a-\zeta_c-\zeta_d)\mathcal{R}_1]\mid l_b\}[(\zeta_a+\zeta_b-\zeta_c-\zeta_d)^{-1}-(-\zeta_a+\zeta_b+\zeta_c+\zeta_d)^{-1}]\\
&+(-1)^{\lambda_2}\{l_d\mid \mathcal{K}_{\lambda_2}(\zeta_d\mathcal{R}_2)\mid\Lambda_2\}\exp[(\zeta_c-\zeta_d)R]E_1[(\zeta_c-\zeta_d)(R+\mathcal{R}_1+\mathcal{R}_2)]\\
&\times\{\Lambda_1\mid \mathcal{K}_{\lambda_1}[(\zeta_a-\zeta_c+\zeta_d)\mathcal{R}_1]\mid l_b\}[(\zeta_a+\zeta_b-\zeta_c+\zeta_d)^{-1}-(-\zeta_a+\zeta_b+\zeta_c-\zeta_d)^{-1}]\big).\end{aligned} \tag{28}$$

Similar arguments can be used to evaluate the rest of $I''_{cd;ab}$. The results are:

$$\begin{aligned}I^{(2)}=(-1)^{l_b+\Lambda_2}&\{l_d\mid \mathcal{K}_{\lambda_2}(\zeta_d\mathcal{R}_2)\mid\Lambda_2\}\big((-1)^{\lambda_1}\{l_b\mid \mathcal{K}_{\lambda_1}(-\zeta_b\mathcal{R}_1)\mid\Lambda_1\}\exp[(\zeta_a+\zeta_b)R]E_1[(\zeta_a+\zeta_b)(R+\mathcal{R}_1)]\\
&\times[(-\zeta_a-\zeta_b+\zeta_c+\zeta_d)^{-1}-(-\zeta_a-\zeta_b+\zeta_c-\zeta_d)^{-1}]+(-1)^{\lambda_1}\{l_b\mid \mathcal{K}_{\lambda_1}(\zeta_b\mathcal{R}_1)\mid\Lambda_1\}\exp[(\zeta_a-\zeta_b)R]\\
&\times E_1[(\zeta_a-\zeta_b)(R+\mathcal{R}_1)][(-\zeta_a+\zeta_b+\zeta_c+\zeta_d)^{-1}-(-\zeta_a+\zeta_b+\zeta_c-\zeta_d)^{-1}]+\exp[(\zeta_c+\zeta_d)R]E_1[(\zeta_c+\zeta_d)(R+\mathcal{R}_1)]\\
&\times\{\Lambda_1\mid \mathcal{K}_{\lambda_1}[(\zeta_a-\zeta_c-\zeta_d)\mathcal{R}_1]\mid l_b\}[(\zeta_a+\zeta_b-\zeta_c-\zeta_d)^{-1}-(-\zeta_a+\zeta_b+\zeta_c+\zeta_d)^{-1}]-\exp[(\zeta_c-\zeta_d)R]\\
&\times E_1[(\zeta_c-\zeta_d)(R+\mathcal{R}_1)]\{\Lambda_1\mid \mathcal{K}_{\lambda_1}[(\zeta_a-\zeta_c+\zeta_d)\mathcal{R}_1]\mid l_b\}[(\zeta_a+\zeta_b-\zeta_c+\zeta_d)^{-1}-(-\zeta_a+\zeta_b+\zeta_c-\zeta_d)^{-1}]\big),\end{aligned} \tag{29}$$

$$\begin{aligned}I^{(3)}=(-1)^{l_d+\Lambda_1}&\{l_b\mid \mathcal{K}_{\lambda_1}(\zeta_b\mathcal{R}_1)\mid\Lambda_1\}\big((-1)^{\lambda_2}\{l_d\mid \mathcal{K}_{\lambda_2}(-\zeta_d\mathcal{R}_2)\mid\Lambda_2\}\exp[(\zeta_c+\zeta_d)R]E_1[(\zeta_c+\zeta_d)(R+\mathcal{R}_2)]\\
&\times[(\zeta_a+\zeta_b-\zeta_c-\zeta_d)^{-1}-(\zeta_a-\zeta_b-\zeta_c-\zeta_d)^{-1}]+(-1)^{\lambda_2}\{l_d\mid \mathcal{K}_{\lambda_2}(\zeta_d\mathcal{R}_2)\mid\Lambda_2\}\exp[(\zeta_c-\zeta_d)R]E_1[(\zeta_c-\zeta_d)(R+\mathcal{R}_2)]\\
&\times[(\zeta_a+\zeta_b-\zeta_c+\zeta_d)^{-1}-(\zeta_a-\zeta_b-\zeta_c+\zeta_d)^{-1}]+\exp[(\zeta_a+\zeta_b)R]E_1[(\zeta_a+\zeta_b)(R+\mathcal{R}_2)]\\
&\times\{\Lambda_2\mid \mathcal{K}_{\lambda_2}[(-\zeta_a-\zeta_b+\zeta_c)\mathcal{R}_2]\mid l_d\}[(-\zeta_a-\zeta_b+\zeta_c+\zeta_d)^{-1}-(\zeta_a+\zeta_b-\zeta_c+\zeta_d)^{-1}]-\exp[(\zeta_a-\zeta_b)R]\\
&\times E_1[(\zeta_a-\zeta_b)(R+\mathcal{R}_2)]\{\Lambda_2\mid \mathcal{K}_{\lambda_2}[(-\zeta_a+\zeta_b+\zeta_c)\mathcal{R}_2]\mid l_d\}[(-\zeta_a+\zeta_b+\zeta_c+\zeta_d)^{-1}-(\zeta_a-\zeta_b-\zeta_c+\zeta_d)^{-1}]\big),\end{aligned} \tag{30}$$

$$\begin{aligned}I^{(4)}=(-1)^{\Lambda_1+\Lambda_2}&\{l_b\mid \mathcal{K}_{\lambda_1}(\zeta_b\mathcal{R}_1)\mid\Lambda_1\}\{l_d\mid \mathcal{K}_{\lambda_2}(\zeta_d\mathcal{R}_2)\mid\Lambda_2\}\big([(-\zeta_a-\zeta_b+\zeta_c+\zeta_d)^{-1}-(-\zeta_a-\zeta_b+\zeta_c-\zeta_d)^{-1}]\\
&\times\exp[(\zeta_a+\zeta_b)R]E_1[(\zeta_a+\zeta_b)R]-[(-\zeta_a+\zeta_b+\zeta_c+\zeta_d)^{-1}-(-\zeta_a+\zeta_b+\zeta_c-\zeta_d)^{-1}]\exp[(\zeta_a-\zeta_b)R]E_1[(\zeta_a-\zeta_b)R]\\
&+[(\zeta_a+\zeta_b-\zeta_c-\zeta_d)^{-1}-(\zeta_a-\zeta_b-\zeta_c-\zeta_d)^{-1}]\exp[(\zeta_c+\zeta_d)R]E_1[(\zeta_c+\zeta_d)R]-[(\zeta_a+\zeta_d-\zeta_c+\zeta_d)^{-1}\\
&-(\zeta_a-\zeta_b-\zeta_c+\zeta_d)^{-1}]\exp[(\zeta_c-\zeta_d)R]E_1[(\zeta_c-\zeta_d)R]\big).\end{aligned} \tag{31}$$

DISCUSSION OF APPARENT SINGULARITIES

The four-center integral, as given by Eqs. (1), (2), (12), (17), (20), and (28)–(31), has cancelling singularities when some combinations of ζ's vanish. In such cases the formulas must be modified to remove the singularities before they can be used numerically.

It is easily shown that the logarithmic singularities in $E_1[(\zeta_a-\zeta_b)G]$ and $E_1[(\zeta_c-\zeta_d)G]$, where G is a sum of R's, are not really there; i.e., $E_1[(\zeta_a-\zeta_b)G]$ can be replaced by

$$\tilde{E}_1[(\zeta_a-\zeta_b)G]-\log G, \tag{32}$$

and similarly for $E_1[(\zeta_c-\zeta_d)G]$.

A different kind of apparent singularity is exhibited by

$$\{\Lambda_2\mid \mathcal{K}_{\lambda_2}[(-\zeta_a-\zeta_b+\zeta_c)\mathcal{R}_2\mid l_d\}[(-\zeta_a-\zeta_b+\zeta_c+\zeta_d)^{-1}-(\zeta_a+\zeta_b-\zeta_c+\zeta_d)^{-1}], \tag{33}$$

which appears several times in $I''_{cd;ab}$ [see Eqs. (20) and (28)–(30)], when $\zeta_c-\zeta_a-\zeta_b\sim 0$. Set $z=\zeta_c-\zeta_a-\zeta_b$. To evaluate (33) when $z\sim 0$, expand $(\zeta\pm z)^{-1}$ in a Taylor series in z, then take derivatives with respect to the ζ's. Dropping the subscripts for clarity, we obtain

$$\{\Lambda\mid \mathcal{K}_\lambda(z\mathcal{R})\mid l\}[(\zeta+z)^{-1}-(\zeta-x)^{-1}]=-2\sum_{m=0}^{\infty}\left(\frac{1}{z}\frac{d}{dz}\right)^{\Lambda} z^{1+\Lambda+l}\mathcal{K}_\lambda(z\mathcal{R})\,z^{2m}\zeta^{-2m-2l-2}\,\frac{(2m+2l)!!}{(2m)!!}. \tag{34}$$

Possible singularities in (34) can come only from odd terms in the Laurent expansion of $z^{1+\Lambda+l}\mathcal{K}_\lambda(z\mathcal{R})$. The first odd term in the expansion of Eq. (34) is

$$2(z^{-1}d/dz)^{\Lambda}(2l)!!(-\mathcal{R})^{\lambda}[(2\lambda+1)!!]^{-1}z^{1+\Lambda+l+\lambda}\zeta^{-2l-2}. \tag{35}$$

The $c^{\lambda}(lm,\Lambda M)$ [Eqs. (11) and (17)] require $\Lambda+l+\lambda$ to be even, and $\lambda\geq|\Lambda-l|$. Thus

$$\Lambda+l+\lambda+1\geq\Lambda+l+|\Lambda-l|+1 \tag{36}$$

$$>2\Lambda, \tag{37}$$

which indicates that Eqs. (34) and (35) are not singular at $z=0$. To summarize, when a combination of three ζ's appearing in a $\mathcal{K}_\lambda$ function is near zero, Eqs. (28)–(30) must be modified by expanding in a Taylor series with respect to this combination and keeping the first few terms which survive the differentiations.

A third type of apparent singularity occurs when a sum of four ζ's vanishes. Consider, for instance the term in $I^{(1)}$ [Eqs. (28)],

$$\begin{aligned}J\equiv{}&(-1)^{l_b+l_d+\lambda_1}\{l_b\mid\mathcal{K}_{\lambda_1}(-\zeta_b\mathcal{R}_1)\mid\Lambda_1\}\exp[(\zeta_a+\zeta_b)R]E_1[(\zeta_a+\zeta_b)(R+\mathcal{R}_1+\mathcal{R}_2)]\\&\times\{\Lambda_2\mid\mathcal{K}_{\lambda_2}[(-\zeta_a-\zeta_b+\zeta_c)\mathcal{R}_2]\mid l_d\}(-\zeta_a-\zeta_b+\zeta_c+\zeta_d)^{-1}+(-1)^{l_b+l_d+\lambda_2}\{l_d\mid\mathcal{K}_{\lambda_2}(-\zeta_d\mathcal{R}_2)\mid\Lambda_2\}\\&\times\exp[(\zeta_c+\zeta_d)R]E_1[(\zeta_c+\zeta_d)(R+\mathcal{R}_1+\mathcal{R}_2)]\{\Lambda_1\mid\mathcal{K}_{\lambda_1}[(\zeta_a-\zeta_c-\zeta_d)\mathcal{R}_1]\mid l_b\}(\zeta_a+\zeta_b-\zeta_c-\zeta_d)^{-1},\end{aligned} \tag{38}$$

when $\zeta_a+\zeta_b-\zeta_c-\zeta_d\sim 0$. In this situation two distinct poles in the integrand of Eq. (21) have coalesced. The appropriate part of Eq. (21), equivalent to Eq. (38), is

$$\begin{aligned}J={}&(-1)^{l_b+l_d}(2\pi i)^{-1}\int_{\infty\exp(i\epsilon)}^{(0+)}du\,\log(-u)\,\exp(-Ru)\,(\{\Lambda_1\mid\mathcal{K}_{\lambda_1}[(\zeta_a+u)\mathcal{R}_1]\mid l_b\}(\zeta_a+\zeta_b+u)^{-1})\\&\times(\{\Lambda_2\mid\mathcal{K}_{\lambda_2}[(\zeta_c+u)\mathcal{R}_2]\mid l_d\}(\zeta_c+\zeta_d+u)^{-1}).\end{aligned} \tag{39}$$

To evaluate Eq. (39) when $\zeta_a+\zeta_b-\zeta_c-\zeta_d\sim 0$, use

$$(\zeta_c+\zeta_d+u)^{-1}=\sum_{s=0}^{\infty}(\zeta_a+\zeta_b-\zeta_c-\zeta_d)^{s}(\zeta_a+\zeta_b+u)^{-s-1}, \tag{40}$$

then use Eq. (25) and the residue theorem to obtain

$$\begin{aligned}J={}&(-1)^{l_b+l_d}\sum_{s=0}^{\infty}[(\Lambda_1+\Lambda_2+l_b+l_d+s+1)!]^{-1}\left(\frac{d}{du}\right)_{u=-\zeta_a-\zeta_b}^{\Lambda_1+\Lambda_2+l_b+l_d+s+1}(\zeta_a+\zeta_b+u)^{\Lambda_1+\Lambda_2+l_b+l_d+s+2}\\&\times E_1[-u(R+\mathcal{R}_1+\mathcal{R}_2)]\exp(-uR)(\{\Lambda_1\mid\mathcal{K}_{\lambda_1}[(\zeta_a+u)\mathcal{R}_1]\mid l_b\}(\zeta_a+\zeta_b+u)^{-1})\\&\times(\{\Lambda_2\mid\mathcal{K}_{\lambda_2}[(\zeta_c+u)\mathcal{R}_2]\mid l_d\}(\zeta_a+\zeta_b+u)^{-s-1}(\zeta_a+\zeta_b-\zeta_c-\zeta_d)^{s}).\end{aligned} \tag{41}$$

CONVERGENCE

To grapple with the convergence of Eq. (12) is a difficult matter. The series does not seem to be absolutely convergent. Provided that all l-type summations are carried out before the i, j, k summations, one can prove in general that convergence is at least as fast as $N^{-1/2}$, where $i, j, k\leq N$. In the case of a specific two-center nuclear attraction integral treated by the same method, we could prove that the convergence is like N^{-1}. (Note that in two-center cases i, j, and k collapse to a single index.) Explicit computations for this specific case confirmed the N^{-1} convergence.

CONCLUSION

The four-center integral of r_{12}^{-1} with Slater-type orbitals has been evaluated via the Taylor series expansion of r_{12}^{-1}. The formulas obtained are valid for arbitrary orbital exponents and general values of the n, l, m parameters, but care must be taken to cancel singularities for certain values of the orbital exponents. The formulas do not have the multiregion form[1–4] shown by the integrals when evaluated by the Fourier-transform method. The price of a single all-region formula is additional infinite summations. Formulas for the case when one or more of the internuclear distances vanish can be obtained by letting the appropriate R's go to zero in the four-center formulas (with due care to cancellation of singularities).

ACKNOWLEDGMENT

The authors thank Mr. H. David Todd for computationally confirming the convergence rate of a two-center nuclear attraction integral.

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 51, NUMBER 3 1 AUGUST 1969

Infrared Spectra of Carbon Monoxide in Zeolites*

P. J. Fenelon and H. E. Rubalcava†
Department of Chemistry, University College, Dublin 4, Ireland
(Received 15 October 1968)

The infrared spectra of $^{12}C^{16}O$ and of a mixture of $^{12}C^{16}O$ and $^{13}C^{16}O$ in the zeolite NaA show bands that have been assigned as R-, Q-, and P-branch maxima of a relatively free rotor. This conclusion depends, partly, on small but experimentally distinguishable differences in the isotope shift of the bands of a pure vibrator and those of a vibrotor. The spectrum of carbon monoxide in the zeolite NaX is similar to that in NaA. However, in CaA, and in CaX, where it is known that CO is more strongly adsorbed than in the sodium zeolites, the bands have a different structure, corresponding to a strongly hindered rotor.

INTRODUCTION

As environments for spectroscopic studies of the effect of environment on molecular energy levels, the zeolites have at least one feature that distinguishes them from other host materials such as noble-gas matrices and alkali halide crystals: The cavities in the zeolites that hold the guest molecules have a diameter which is more than twice that of small guest molecules such as carbon monoxide. Thus, one may expect that in zeolites the energy levels of entrapped small molecules will be subject to less severe perturbations than those which act on probe molecules in more familiar matrices for which the ratio of the molecular diameter to the site diameter is about one. For such smaller perturbations the resulting spectrum would be intermediate in character between that of the unperturbed molecules as in the gas phase, and that of the relatively strongly perturbed molecules as in a noble-gas matrix.[1] We believe these expectations are realized for carbon monoxide in sodium zeolite type A and type X. The infrared spectrum of carbon monoxide shows a structure that is plausibly interpreted as arising from transitions between the energy levels of a vibrotor perturbed by collisions with the cage walls. In some respects, this structure resembles more closely that observed for molecules in the gas phase than it does those of carbon monoxide in the liquid phase,[2] or in various solid matrices.[1,3]

Recently, Angell and Schaffer[4] have reported an investigation of the spectra of carbon monoxide in several X-type and Y-type zeolites; for some zeolites they observed as many as three bands due to the entrapped carbon monoxide molecules. They showed convincingly that, for zeolites containing multicharged cations, the band at highest frequency is due to molecules adsorbed on those cations, and that the two bands at lower frequencies appear for all zeolites. Although the latter two bands resemble unresolved R- and P-branch maxima, Angell and Schaffer did not assign them as such because the band intensities did not

* Presented in part at the Joint Annual Meeting of the Chemical Society, the Institute of Chemistry of Ireland, and the Royal Institute of Chemistry, held at University College, Dublin, April 1968.
† To whom correspondence regarding this paper should be sent.
[1] G. E. Leroi, G. E. Ewing, and G. C. Pimentel, J. Chem. Phys. **40**, 2298 (1964).
[2] G. E. Ewing, J. Chem. Phys. **37**, 2250 (1962).
[3] A. G. Maki, J. Chem. Phys. **35**, 931 (1961).
[4] C. L. Angell and P. C. Schaffer, J. Phys. Chem. **70**, 1413 (1966).