Four-center Integral of a Dipolar Two-electron Potential Between s-type GTO's

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We reduce two-electron 4-center products of Cartesian Gaussian Type Orbitals with Boys' contraction to 2-center products of the form $\psi_\alpha(\mathbf{r}_i - \mathbf{A})\ \psi_\beta(\mathbf{r}_j - \mathbf{B})$, and compute the 6-dimensional integral over $d^3r_i d^3r_j$ over these with the effective potential $V_{ij} = (\mathbf{r}_i - \mathbf{r}_j)\cdot\mathbf{r}_j/|\mathbf{r}_i - \mathbf{r}_j|^3$.

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I. FORMAT OF THE TASK

In relativistic quantum chemistry, the effective electron-electron interaction contains so-called gauge correction terms [1–3] which appear in the theory of quantum chemistry as energy terms of the form

$$J(\alpha, \mathbf{A}, \beta, \mathbf{B}, \gamma, \mathbf{C}, \delta, \mathbf{D}) = \int d^3r_i d^3r_j \psi_\alpha(\mathbf{r}_i - \mathbf{A})\psi_\beta(\mathbf{r}_i - \mathbf{B})\frac{(\mathbf{r}_i - \mathbf{r}_j)\cdot(2\mathbf{r}_i - \mathbf{r}_j)}{|\mathbf{r}_i - \mathbf{r}_j|^3}\psi_\gamma(\mathbf{r}_j - \mathbf{C})\psi_\delta(\mathbf{r}_j - \mathbf{D}) \tag{1}$$

for orbitals ψ centered at places $\mathbf{A}$, $\mathbf{B}$, $\mathbf{C}$ and $\mathbf{D}$. The Gauss Transformation Method has been shown to calculate the integral if the orbitals ψ are expanded in a basis of Gaussian Type Orbitals (GTO's) [4]; this manuscript basically demonstrates how dealing with the quadratic forms in the exponentials directly also manages to reduce them to the omnipresent Confluent Hypergeometric Functions of the electron repulsion integrals (ERI's).

II. REDUCTION TO 2-CENTER INTEGRALS

As usual for GTO's [5] we contract the Gaussians by defining intermediate centers $\mathbf{P}$ and $\mathbf{Q}$:

$$\mathbf{P} \equiv \frac{\alpha\mathbf{A} + \beta\mathbf{B}}{\alpha + \beta}, \tag{2}$$

$$\mathbf{Q} \equiv \frac{\gamma\mathbf{C} + \delta\mathbf{D}}{\gamma + \delta}, \tag{3}$$

$$e^{-\alpha(\mathbf{r}-\mathbf{A})^2}e^{-\beta(\mathbf{r}-\mathbf{B})^2} = \exp[-\frac{\alpha\beta}{\alpha+\beta}(\mathbf{A}-\mathbf{B})^2]e^{-(\alpha+\beta)(\mathbf{r}-\mathbf{P})^2}, \tag{4}$$

$$e^{-\gamma(\mathbf{r}-\mathbf{C})^2}e^{-\delta(\mathbf{r}-\mathbf{D})^2} = \exp[-\frac{\gamma\delta}{\gamma+\delta}(\mathbf{C}-\mathbf{D})^2]e^{-(\gamma+\delta)(\mathbf{r}-\mathbf{Q})^2}. \tag{5}$$

The same is done for the prefactors for p, d-type integrals, so the integrals are actually 2-center integrals:

$$\bar{J} \equiv \exp[-\frac{\alpha\beta}{\alpha+\beta}(\mathbf{A}-\mathbf{B})^2 - \frac{\gamma\delta}{\gamma+\delta}(\mathbf{C}-\mathbf{D})^2]I(\kappa, \mathbf{P}, \lambda, \mathbf{Q}), \tag{6}$$

where

$$I(\kappa, \mathbf{P}, \lambda, \mathbf{Q}) \equiv \int d^3r_i d^3r_j \psi_\kappa(\mathbf{r}_i - \mathbf{P})\frac{(\mathbf{r}_i - \mathbf{r}_j)\cdot(2\mathbf{r}_i - \mathbf{r}_j)}{|\mathbf{r}_i - \mathbf{r}_j|^3}\psi_\lambda(\mathbf{r}_j - \mathbf{Q}). \tag{7}$$

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III. REDUCTION TO TRIPLE INTEGRAL

The substitution $\mathbf{R} = \mathbf{r}_i - \mathbf{r}_j$ in the integrand yields

$$I = \int d^3R d^3r_j \psi_\kappa(\mathbf{R} + \mathbf{r}_j - \mathbf{P}) \frac{\mathbf{R}\cdot(\mathbf{R}+\mathbf{r}_j)}{R^3} \psi_\lambda(\mathbf{r}_j - \mathbf{Q}). \tag{8}$$

Because the first term

$$\int d^3R d^3r_j \psi_\kappa(\mathbf{R} + \mathbf{r}_j - \mathbf{P}) \frac{\mathbf{R}\cdot\mathbf{R}}{R^3} \psi_\lambda(\mathbf{r}_j - \mathbf{Q}) = \int d^3R d^3r_j \psi_\kappa(\mathbf{R} + \mathbf{r}_j - \mathbf{P}) \frac{1}{R} \psi_\lambda(\mathbf{r}_j - \mathbf{Q}) \tag{9}$$

of I is the usual 2-electron Coulomb repulsion [6], the entire focus of this manuscript is on the second term,

$$\bar{I}(\kappa, \mathbf{P}, \lambda, \mathbf{Q}) \equiv \int d^3R d^3r_j \psi_\kappa(\mathbf{R} + \mathbf{r}_j - \mathbf{P}) \frac{\mathbf{R}\cdot\mathbf{r}_j}{R^3} \psi_\lambda(\mathbf{r}_j - \mathbf{Q}). \tag{10}$$

For s-type orbitals along the Cartesian coordinates $\mathbf{r}_j = (r_x, r_y, r_z)$ the dot products are expanded which decomposes the dot product into a sum of three contributions:

$$\begin{aligned}
\bar{I}(\kappa, \mathbf{P}, \lambda, \mathbf{Q}) &= e^{-\kappa P^2 - \lambda Q^2} \int dr_x dr_y dr_z dR_x dR_y dR_z \\
&\quad \times e^{-\kappa[R_x^2+R_y^2+R_z^2+r_x^2+r_y^2+r_z^2+2R_xr_x+2R_yr_y+2R_zr_z-2R_xP_x-2R_yP_y-2R_zP_z-2r_xP_x-2r_yP_y-2r_zP_z]} \\
&\quad \times \frac{R_xr_x + R_yr_y + R_zr_z}{(R_x^2+R_y^2+R_z^2)^{3/2}} e^{-\lambda[r_x^2+r_y^2+r_z^2-2r_xQ_x-2r_yQ_y-2r_zQ_z]} \\
&= e^{-\kappa P^2 - \lambda Q^2} \Big[\int dr_x dr_y dr_z dR_x dR_y dR_z e^{-\kappa[R_x^2+R_y^2+R_z^2+r_x^2+r_y^2+r_z^2+2R_xr_x+2R_yr_y+2R_zr_z-2R_xP_x-2R_yP_y-2R_zP_z-2r_xP_x-2r_yP_y-2r_zP_z]} \\
&\quad \times \frac{R_xr_x}{(R_x^2+R_y^2+R_z^2)^{3/2}} e^{-\lambda[r_x^2+r_y^2+r_z^2-2r_xQ_x-2r_yQ_y-2r_zQ_z]} \\
&\quad + \int dr_x dr_y dr_z dR_x dR_y dR_z e^{-\kappa[R_x^2+R_y^2+R_z^2+r_x^2+r_y^2+r_z^2+2R_xr_x+2R_yr_y+2R_zr_z-2R_xP_x-2R_yP_y-2R_zP_z-2r_xP_x-2r_yP_y-2r_zP_z]} \\
&\quad \times \frac{R_yr_y}{(R_x^2+R_y^2+R_z^2)^{3/2}} e^{-\lambda[r_x^2+r_y^2+r_z^2-2r_xQ_x-2r_yQ_y-2r_zQ_z]} \\
&\quad + \int dr_x dr_y dr_z dR_x dR_y dR_z e^{-\kappa[R_x^2+R_y^2+R_z^2+r_x^2+r_y^2+r_z^2+2R_xr_x+2R_yr_y+2R_zr_z-2R_xP_x-2R_yP_y-2R_zP_z-2r_xP_x-2r_yP_y-2r_zP_z]} \\
&\quad \times \frac{R_zr_z}{(R_x^2+R_y^2+R_z^2)^{3/2}} e^{-\lambda[r_x^2+r_y^2+r_z^2-2r_xQ_x-2r_yQ_y-2r_zQ_z]} \Big] \\
&= e^{-\kappa P^2 - \lambda Q^2} \Big[\int dr_x dR_x \int dr_y dR_y \int dr_z dR_z e^{-\kappa[R_x^2+r_x^2+2R_xr_x-2R_xP_x-2r_xP_x]} \\
&\quad \times e^{-\kappa[R_y^2+r_y^2+2R_yr_y-2R_yP_y-2r_yP_y]} \\
&\quad \times e^{-\kappa[R_z^2+r_z^2+2R_zr_z-2R_zP_z-2r_zP_z]} \\
&\quad \times \frac{R_xr_x}{(R_x^2+R_y^2+R_z^2)^{3/2}} e^{-\lambda[r_x^2-2r_xQ_x]} e^{-\lambda[r_y^2-2r_yQ_y]} e^{-\lambda[r_z^2-2r_zQ_z]} \\
&\quad + (x \to y) + (x \to z) \Big] \\
&= e^{-\kappa P^2 - \lambda Q^2} \Big[\int dr_x dR_x e^{-\kappa[R_x^2+r_x^2+2R_xr_x-2R_xP_x-2r_xP_x]} \frac{R_xr_x}{(R_x^2+R_y^2+R_z^2)^{3/2}} e^{-\lambda[r_x^2-2r_xQ_x]} \\
&\quad \times \int dr_y dR_y e^{-\kappa[R_y^2+r_y^2+2R_yr_y-2R_yP_y-2r_yP_y]} e^{-\lambda[r_y^2-2r_yQ_y]} \\
&\quad \times \int dr_z dR_z e^{-\kappa[R_z^2+r_z^2+2R_zr_z-2R_zP_z-2r_zP_z]} e^{-\lambda[r_z^2-2r_zQ_z]} \\
&\quad + (x \to y) + (x \to z) \Big].
\end{aligned} \tag{11}$$

The integral over r_z is handled as usual by extension of the quadratic form in the exponential

$$\int dr_z e^{-\kappa[R_z^2+r_z^2+2R_zr_z-2R_zP_z-2r_zP_z]} e^{-\lambda[r_z^2-2r_zQ_z]} = e^{-\kappa[R_z^2-2R_zP_z]}\int dr_z e^{-\kappa[r_z^2+2R_zr_z-2r_zP_z]-\lambda[r_z^2-2r_zQ_z]}$$
$$= e^{-\kappa[R_z^2-2R_zP_z]}\int dr_z e^{-(\kappa+\lambda)r_z^2-2\kappa R_zr_z+2\kappa r_zP_z+2\lambda r_zQ_z} = e^{-\kappa[R_z^2-2R_zP_z]}\int dr_z e^{-(\kappa+\lambda)r_z^2-2(\kappa R_z-\kappa P_z-\lambda Q_z)r_z}$$
$$= e^{-\kappa[R_z^2-2R_zP_z]}\int dr_z e^{-(\kappa+\lambda)[r_z^2+2\frac{\kappa R_z-\kappa P_z-\lambda Q_z}{\kappa+\lambda}r_z]}$$
$$= e^{-\kappa[R_z^2-2R_zP_z]}\int dr_z e^{-(\kappa+\lambda)[r_z^2+2\frac{\kappa R_z-\kappa P_z-\lambda Q_z}{\kappa+\lambda}r_z+(\frac{\kappa R_z-\kappa P_z-\lambda Q_z}{\kappa+\lambda})^2-(\frac{\kappa R_z-\kappa P_z-\lambda Q_z}{\kappa+\lambda})^2]}$$
$$= e^{-\kappa[R_z^2-2R_zP_z]} e^{-(\kappa+\lambda)[-(\frac{\kappa R_z-\kappa P_z-\lambda Q_z}{\kappa+\lambda})^2]}\int dr_z e^{-(\kappa+\lambda)[r_z^2+2\frac{\kappa R_z-\kappa P_z-\lambda Q_z}{\kappa+\lambda}r_z+(\frac{\kappa R_z-\kappa P_z-\lambda Q_z}{\kappa+\lambda})^2]}$$
$$= e^{-\kappa[R_z^2-2R_zP_z]} e^{(\kappa+\lambda)(\frac{\kappa R_z-\kappa P_z-\lambda Q_z}{\kappa+\lambda})^2}\int dr_z e^{-(\kappa+\lambda)r_z^2}$$
$$= e^{-\kappa[R_z^2-2R_zP_z]} e^{\frac{(\kappa R_z-\kappa P_z-\lambda Q_z)^2}{\kappa+\lambda}}\sqrt{\frac{\pi}{\kappa+\lambda}}. \quad (12)$$

The same calculation repeats along the r_y-direction:

$$\int dr_y e^{-\kappa[R_y^2+r_y^2+2R_yr_y-2R_yP_y-2r_yP_y]} e^{-\lambda[r_y^2-2r_yQ_y]} = e^{-\kappa[R_y^2-2R_yP_y]} e^{\frac{(\kappa R_y-\kappa P_y-\lambda Q_y)^2}{\kappa+\lambda}}\sqrt{\frac{\pi}{\kappa+\lambda}}. \quad (13)$$

An additional factor r_x intrudes the integrand along the r_x-direction in (11):

$$\int dr_x r_x e^{-\kappa[R_x^2+r_x^2+2R_xr_x-2R_xP_x-2r_xP_x]} e^{-\lambda[r_x^2-2r_xQ_x]}$$
$$= e^{-\kappa[R_x^2-2R_xP_x]} e^{-(\kappa+\lambda)[-(\frac{\kappa R_x-\kappa P_x-\lambda Q_x}{\kappa+\lambda})^2]}\int dr_x r_x e^{-(\kappa+\lambda)[r_x^2+2\frac{\kappa R_x-\kappa P_x-\lambda Q_x}{\kappa+\lambda}r_x+(\frac{\kappa R_x-\kappa P_x-\lambda Q_x}{\kappa+\lambda})^2]}$$
$$= e^{-\kappa[R_x^2-2R_xP_x]} e^{(\kappa+\lambda)[(\frac{\kappa R_x-\kappa P_x-\lambda Q_x}{\kappa+\lambda})^2]}\int dr_x r_x e^{-(\kappa+\lambda)[r_x+\frac{\kappa R_x-\kappa P_x-\lambda Q_x}{\kappa+\lambda}]^2}$$
$$= e^{-\kappa[R_x^2-2R_xP_x]} e^{(\kappa+\lambda)[(\frac{\kappa R_x-\kappa P_x-\lambda Q_x}{\kappa+\lambda})^2]}\int dt(t-\frac{\kappa R_x-\kappa P_x-\lambda Q_x}{\kappa+\lambda})e^{-(\kappa+\lambda)t^2}$$
$$= -\frac{\kappa R_x-\kappa P_x-\lambda Q_x}{\kappa+\lambda} e^{-\kappa[R_x^2-2R_xP_x]} e^{\frac{(\kappa R_x-\kappa P_x-\lambda Q_x)^2}{\kappa+\lambda}}\int dt e^{-(\kappa+\lambda)t^2}$$
$$= -\frac{\kappa R_x-\kappa P_x-\lambda Q_x}{\kappa+\lambda} e^{-\kappa[R_x^2-2R_xP_x]} e^{\frac{(\kappa R_x-\kappa P_x-\lambda Q_x)^2}{\kappa+\lambda}]}\sqrt{\frac{\pi}{\kappa+\lambda}}. \quad (14)$$

Insertion of the previous three equations into (11) has reduced the 6-fold to a 3-fold integral:

$$\bar{I} = e^{-\kappa P^2-\lambda Q^2}\big[-(\frac{\pi}{\kappa+\lambda})^{3/2}\int dR_x dR_y dR_z \frac{\kappa R_x-\kappa P_x-\lambda Q_x}{\kappa+\lambda} e^{-\kappa[R_x^2-2R_xP_x]} e^{\frac{(\kappa R_x-\kappa P_x-\lambda Q_x)^2}{\kappa+\lambda}}$$
$$\times e^{-\kappa[R_y^2-2R_yP_y]} e^{\frac{(\kappa R_y-\kappa P_y-\lambda Q_y)^2}{\kappa+\lambda}}$$
$$\times e^{-\kappa[R_z^2-2R_zP_z]} e^{\frac{(\kappa R_z-\kappa P_z-\lambda Q_z)^2}{\kappa+\lambda}} \frac{R_x}{(R_x^2+R_y^2+R_z^2)^{3/2}}$$
$$+(x\to y)+(x\to z)\big]. \quad (15)$$

IV. REDUCTION OF THE 1-PARTICLE POTENTIAL

A. Quadratic Form in the Exponential

The principal axis transformation in the Gaussian exponentials with the main variable R_x is

$$e^{-\kappa[R_x^2-2R_xP_x]} e^{\frac{(\kappa R_x-\kappa P_x-\lambda Q_x)^2}{\kappa+\lambda}} = \exp[\kappa P_x^2+\lambda Q_x^2]\exp[-\frac{\kappa\lambda}{\kappa+\lambda}(R_x-P_x+Q_x)^2]. \quad (16)$$

Substitution of this form for R_x, R_y and R_z into (15) produces

$$\begin{aligned}
\bar{I} = e^{-\kappa P^2-\lambda Q^2}\big[-(\frac{\pi}{\kappa+\lambda})^{3/2}\int dR_x dR_y dR_z \frac{\kappa R_x-\kappa P_x-\lambda Q_x}{\kappa+\lambda}\exp[\kappa P_x^2+\lambda Q_x^2]\exp[-\frac{\kappa\lambda}{\kappa+\lambda}(R_x-P_x+Q_x)^2] \\
\times \exp[\kappa P_y^2+\lambda Q_y^2]\exp[-\frac{\kappa\lambda}{\kappa+\lambda}(R_y-P_y+Q_y)^2] \\
\times \exp[\kappa P_z^2+\lambda Q_z^2]\exp[-\frac{\kappa\lambda}{\kappa+\lambda}(R_z-P_z+Q_z)^2]\frac{R_x}{(R_x^2+R_y^2+R_z^2)^{3/2}} \\
+(R_x\to R_y)+(R_x\to R_z)\big] \\
= -(\frac{\pi}{\kappa+\lambda})^{3/2}\int dR_x dR_y dR_z \frac{\kappa R_x-\kappa P_x-\lambda Q_x}{\kappa+\lambda}\exp[-\frac{\kappa\lambda}{\kappa+\lambda}(R_x-P_x+Q_x)^2] \\
\times \exp[-\frac{\kappa\lambda}{\kappa+\lambda}(R_y-P_y+Q_y)^2] \\
\times \exp[-\frac{\kappa\lambda}{\kappa+\lambda}(R_z-P_z+Q_z)^2]\frac{R_x}{(R_x^2+R_y^2+R_z^2)^{3/2}} \\
+(R_x\to R_y)+(R_x\to R_z). \quad (17)
\end{aligned}$$

Definition of new vectors $\mathbf{E}$ and $\mathbf{E}'$ and of a reduced scaling parameter ϵ

$$\mathbf{E}\equiv\mathbf{P}-\mathbf{Q};\quad \epsilon\equiv\frac{\kappa\lambda}{\kappa+\lambda}. \quad (18)$$

$$\mathbf{E}'\equiv\frac{\kappa\mathbf{P}+\lambda\mathbf{Q}}{\kappa+\lambda}; \quad (19)$$

leads back to an integral over the entire space of d^3R:

$$\begin{aligned}
\bar{I} = -(\frac{\pi}{\kappa+\lambda})^{3/2}\int dR_x dR_y dR_z \frac{\kappa R_x-\kappa P_x-\lambda Q_x}{\kappa+\lambda}\exp[-\frac{\kappa\lambda}{\kappa+\lambda}(\mathbf{R}-\mathbf{E})^2]\frac{R_x}{(R_x^2+R_y^2+R_z^2)^{3/2}} \\
+(R_x\to R_y)+(R_x\to R_z) \\
= -(\frac{\pi}{\kappa+\lambda})^{3/2}\int dR_x dR_y dR_z \frac{\kappa\mathbf{R}\cdot\mathbf{R}-(\kappa\mathbf{P}+\lambda\mathbf{Q})\cdot\mathbf{R}}{\kappa+\lambda}\exp[-\epsilon(\mathbf{R}-\mathbf{E})^2]\frac{1}{(R_x^2+R_y^2+R_z^2)^{3/2}}. \quad (20)
\end{aligned}$$

The exponent in this integrand involves the cosine of the angle between the vectors $\mathbf{R}$ and $\mathbf{E}$:

$$\exp[-\epsilon(\mathbf{R}-\mathbf{E})^2]=\exp[-\epsilon\{R^2+E^2-2ER(\sin\theta\sin\theta_E\cos(\phi-\phi_E)+\cos\theta\cos\theta_E)\}] \quad (21)$$

supposed we define the polar and azimuthal angles

$$\mathbf{R}=R(\sin\theta\cos\phi,\sin\theta\sin\phi,\cos\theta); \quad (22)$$

$$\mathbf{E}=E(\sin\theta_E\cos\phi_E,\sin\theta_E\sin\phi_E,\cos\theta_E). \quad (23)$$

As the only noticeable idea in this calculation, we apply the inverse coordinate transformation (A5) such that the z coordinate of the new coordinate system points towards $\mathbf{E}$, so the cosine in the dot product $\mathbf{R}\cdot\mathbf{E}$ is just the cosine of the polar coordinate of $\mathbf{X}$ in the new coordinate system observed in (A2):

$$\mathbf{R}=\mathbf{\Omega}^{-1}\mathbf{X}; \quad (24)$$

$$\mathbf{R}\cdot\mathbf{E}=\mathbf{\Omega}^{-1}\mathbf{X}\cdot\mathbf{E}=\mathbf{X}\cdot\mathbf{\Omega}\mathbf{E}. \quad (25)$$

$$\mathbf{\Omega}^{-1}=\begin{pmatrix} (1-\cos\theta_E)\sin^2\phi_E+\cos\theta_E & -(1-\cos\theta_E)\sin\phi_E\cos\phi_E & \sin\theta_E\cos\phi_E \\ -(1-\cos\theta_E)\cos\phi_E\sin\phi_E & (1-\cos\theta_E)\cos^2\phi_E+\cos\theta_E & \sin\theta_E\sin\phi_E \\ -\sin\theta_E\cos\phi_E & -\sin\theta_E\sin\phi_E & \cos\theta_E \end{pmatrix}. \quad (26)$$

The rotation preserves lengths, $R=|\mathbf{R}|=X=|\mathbf{X}|$.

$$\bar{I}=-(\frac{\pi}{\kappa+\lambda})^{3/2}\int dX_xdX_ydX_z\frac{\kappa\mathbf{X}\cdot\mathbf{X}-(\kappa\mathbf{P}+\lambda\mathbf{Q})\cdot\mathbf{\Omega}^{-1}\mathbf{X}}{\kappa+\lambda}\exp[-\frac{\kappa\lambda}{\kappa+\lambda}(\mathbf{\Omega}^{-1}\mathbf{X}-\mathbf{E})^2]\frac{1}{(X_x^2+X_y^2+X_z^2)^{3/2}} \tag{27}$$

$$=-(\frac{\pi}{\kappa+\lambda})^{3/2}\int dX_xdX_ydX_z(\frac{\kappa}{\kappa+\lambda}X^2-\mathbf{E}'\cdot\mathbf{\Omega}^{-1}\mathbf{X})\exp[-\frac{\kappa\lambda}{\kappa+\lambda}(\mathbf{\Omega}^{-1}\mathbf{X}-\mathbf{E})^2]\frac{1}{(X_x^2+X_y^2+X_z^2)^{3/2}} \tag{28}$$

$$=-(\frac{\pi}{\kappa+\lambda})^{3/2}[\frac{\kappa}{\kappa+\lambda}\bar{I}_1-\bar{I}_2] \tag{29}$$

B. Isotropic Part

The term $\bar{I}_1$ involves a factor $X^2\sin\theta$ from the Jacobian in spherical coordinates, a factor $\mathbf{X}\cdot\mathbf{X}=X^2$ from the dot product, and the dipolar $1/X^3$ in the denominator:

$$\begin{aligned}\bar{I}_1(\epsilon,\mathbf{E}) &= \int dX_xdX_ydX_zX^2\exp[-\epsilon(\mathbf{X}-\mathbf{E})^2]\frac{1}{(X_x^2+X_y^2+X_z^2)^{3/2}}\\
&= e^{-\epsilon E^2}\int X^2\sin\theta dXd\theta d\phi X^2\exp[-\epsilon\{X^2-2EX\cos\theta\}]\frac{1}{(X_x^2+X_y^2+X_z^2)^{3/2}}\\
&= e^{-\epsilon E^2}\int X\sin\theta dXd\theta d\phi\exp[-\epsilon\{X^2-2EX\cos\theta\}]\\
&= 2\pi e^{-\epsilon E^2}\int X\sin\theta dXd\theta\exp[-\epsilon\{X^2-2EX\cos\theta\}]\\
&= 2\pi e^{-\epsilon E^2}\int XdX\int_{-1}^{1}dz\exp[-\epsilon\{X^2-2EXz\}]\\
&= 2\pi e^{-\epsilon E^2}\int_0^\infty XdXe^{-\epsilon X^2}\int_{-1}^{1}dz\exp[2\epsilon EXz]\\
&= 2\pi e^{-\epsilon E^2}\int_0^\infty XdXe^{-\epsilon X^2}\frac{1}{2\epsilon EX}(e^{2\epsilon EX}-e^{-2\epsilon EX})\\
&= \frac{\pi}{\epsilon E}e^{-\epsilon E^2}\int_0^\infty dXe^{-\epsilon X^2}(e^{2\epsilon EX}-e^{-2\epsilon EX})\\
&= \frac{\pi}{2\epsilon^2E^2}e^{-\epsilon E^2}\int_0^\infty dte^{-t^2/(4\epsilon E^2)}(e^t-e^{-t})=\frac{2\pi}{\epsilon}F_0(\epsilon E^2).\end{aligned} \tag{30}$$

The function F_0 is made more explicit in Appendix B. The gradient with respect to $\mathbf{E}$ is an application of (D2):

$$\nabla_{\mathbf{E}}\bar{I}_1=-4\pi F_1(\epsilon E^2)\mathbf{E}. \tag{31}$$

This indicates that working out the integrals for 4-center orbitals beyond the $(0,0,0)$-triple of "orbital" quantum numbers through repeated differentiation with respect to the locations of the four centers [7, 8] poses no further problems.

C. Dipolar Part

In the other integral

$$\bar{I}_2=\int d^3X\mathbf{E}'\cdot\mathbf{\Omega}^{-1}\mathbf{X}\exp[-\epsilon(\mathbf{\Omega}^{-1}\mathbf{X}-\mathbf{E})^2]\frac{1}{X^3}$$

we rather compute three components defined by moving the $\mathbf{\Omega}$ operator to the compound vector $\mathbf{E}'$:

$$\mathbf{E}'\cdot\mathbf{\Omega}^{-1}\mathbf{X}=\mathbf{\Omega}\mathbf{E}'\cdot\mathbf{X}=H_xX_x+H_yX_y+H_zX_z \tag{32}$$

where we have defined the vector $\mathbf{H} \equiv \mathbf{\Omega}\mathbf{E}'$.

$$\bar{I}_2 = H_x \bar{I}_{2x} + H_y \bar{I}_{2y} + H_z \bar{I}_{2z}. \tag{33}$$

Its z-component is obtained with (A5)

$$H_z = \frac{1}{E}\mathbf{E}\cdot\mathbf{E}'. \tag{34}$$

The integrals $\bar{I}_{2x}$ and $\bar{I}_{2y}$ vanish once integrated over the azimuth ϕ:

$$\bar{I}_{2x} = \int dX_x dX_y dX_z X_x \exp[-\frac{\kappa\lambda}{\kappa+\lambda}(\mathbf{\Omega}^{-1}\mathbf{X}-\mathbf{E})^2]\frac{1}{(X_x^2+X_y^2+X_z^2)^{3/2}}$$
$$= e^{-\epsilon E^2}\int dX \sin\theta d\theta d\phi \cos\phi \sin\theta \exp[-\epsilon\{X^2-2EX\cos\theta\}] = 0. \tag{35}$$

$$\bar{I}_{2y} = \int dX_x dX_y dX_z X_y \exp[-\frac{\kappa\lambda}{\kappa+\lambda}(\mathbf{\Omega}^{-1}\mathbf{X}-\mathbf{E})^2]\frac{1}{(X_x^2+X_y^2+X_z^2)^{3/2}}$$
$$= e^{-\epsilon E^2}\int dX \sin\theta d\theta d\phi \sin\phi \sin\theta \exp[-\epsilon\{X^2-2EX\cos\theta\}] = 0. \tag{36}$$

The only finite contribution is from the component coupled to H_z:

$$\bar{I}_{2z}(\epsilon,\mathbf{E}) = \int dX_x dX_y dX_z X_z \exp[-\frac{\kappa\lambda}{\kappa+\lambda}(\mathbf{\Omega}^{-1}\mathbf{X}-\mathbf{E})^2]\frac{1}{(X_x^2+X_y^2+X_z^2)^{3/2}}$$
$$= e^{-\epsilon E^2}\int dX \sin\theta d\theta d\phi \cos\theta \exp[-\epsilon\{X^2-2EX\cos\theta\}]$$
$$= 2\pi e^{-\epsilon E^2}\int dX \sin\theta d\theta \cos\theta \exp[-\epsilon\{X^2-2EX\cos\theta\}]$$
$$= 2\pi e^{-\epsilon E^2}\int_0^\infty dX \int_{-1}^1 dt t \exp[-\epsilon\{X^2-2EXt\}]$$
$$= 2\pi e^{-\epsilon E^2}\int_0^\infty dX e^{-\epsilon X^2}\int_{-1}^1 dt t \exp[2\epsilon EXt]$$
$$= 2\pi e^{-\epsilon E^2}\int_0^\infty dX e^{-\epsilon X^2}\frac{1}{(2\epsilon EX)^2}[e^{2\epsilon EX}(2\epsilon EX-1)+e^{-2\epsilon EX}(2\epsilon EX+1)]$$
$$= 2\pi e^{-\epsilon E^2}\frac{1}{2\epsilon E}\int_0^\infty dt e^{-t^2/(4\epsilon E^2)}\frac{1}{t^2}[e^t(t-1)+e^{-t}(t+1)] = 4\pi E F_1(\epsilon E^2). \tag{37}$$

The auxiliary special function F_1 is computed via the error function in Appendix C. The gradient with respect to $\mathbf{E}$ is an application of (D2) and of the product rule of differentiation:

$$\nabla_{\mathbf{E}}\bar{I}_{2z} = \frac{4\pi}{E}[F_1(\epsilon E^2) - 2\epsilon E^2 F_2(\epsilon E^2)]\mathbf{E}. \tag{38}$$

V. SUMMARY

In numerical practise the steps of the obtaining J are:

1. Define the intermediate centers $\mathbf{P}$ and $\mathbf{Q}$ with their effective scaling factors $\kappa+\beta$ and $\lambda+\delta$;
2. Calculate the exponential pre-factor in (6);
3. Calculate the dropped contribution (9) by any other library;
4. Calculate the contribution $\bar{I}$ from (29):
   (a) Implement Shavitt's functions F_0 and F_1 for positive real-valued arguments;
   (b) Calculate the two vectors and parameter in (18)-(19);
   (c) Calculate $\bar{I}_2$ as the product of H_z in (34) and $\bar{I}_{2z}$ in (37).
   (d) Calculate $\bar{I}_1$ in (30).

Appendix A: Coordinate rotation

The orthogonal unimodular 3×3 matrix which rotates points by an angle θ_E around the right-handed axis with Cartesian coordinates $(\omega_1, \omega_2, \omega_3)$, normalized to unit length $\omega_1^2 + \omega_2^2 + \omega_3^2 = 1$, is [9][10, (2.21)]

$$\mathbf{\Omega} = \begin{pmatrix} (1-\cos\theta_E)\omega_1^2 + \cos\theta_E & (1-\cos\theta_E)\omega_1\omega_2 - \sin\theta_E\omega_3 & (1-\cos\theta_E)\omega_1\omega_3 + \sin\theta_E\omega_2 \\ (1-\cos\theta_E)\omega_1\omega_2 + \sin\theta_E\omega_3 & (1-\cos\theta_E)\omega_2^2 + \cos\theta_E & (1-\cos\theta_E)\omega_2\omega_3 - \sin\theta_E\omega_1 \\ (1-\cos\theta_E)\omega_1\omega_3 - \sin\theta_E\omega_2 & (1-\cos\theta_E)\omega_2\omega_3 + \sin\theta_E\omega_1 & (1-\cos\theta_E)\omega_3^2 + \cos\theta_E \end{pmatrix}. \tag{A1}$$

We wish to find the axis that rotates the Cartesian vector (23) to the image $E(0, 0, 1)$, such that

$$\mathbf{\Omega} \cdot \begin{pmatrix} \cos\phi_E \sin\theta_E \\ \sin\phi_E \sin\theta_E \\ \cos\theta_E \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}. \tag{A2}$$

The rotation axis is the cross product between the point in space and its image:

$$\begin{pmatrix} \cos\phi_E \sin\theta_E \\ \sin\phi_E \sin\theta_E \\ \cos\theta_E \end{pmatrix} \times \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} = \begin{pmatrix} \sin\phi_E \sin\theta_E \\ -\cos\phi_E \sin\theta_E \\ 0 \end{pmatrix}. \tag{A3}$$

Normalized to unit length it constructs the axis vector ω with Cartesian components

$$\begin{pmatrix} \omega_1 \\ \omega_2 \\ \omega_3 \end{pmatrix} = \begin{pmatrix} \sin\phi_E \\ -\cos\phi_E \\ 0 \end{pmatrix}. \tag{A4}$$

Insertion into (A1) yields the rotation matrix applicable to (A2):

$$\mathbf{\Omega} = \begin{pmatrix} (1-\cos\theta_E)\sin^2\phi_E + \cos\theta_E & -(1-\cos\theta_E)\sin\phi_E\cos\phi_E & -\sin\theta_E\cos\phi_E \\ -(1-\cos\theta_E)\cos\phi_E\sin\phi_E & (1-\cos\theta_E)\cos^2\phi_E + \cos\theta_E & -\sin\theta_E\sin\phi_E \\ \sin\theta_E\cos\phi_E & \sin\theta_E\sin\phi_E & \cos\theta_E \end{pmatrix}. \tag{A5}$$

The inverse rotation is represented by the inverse matrix (which equals the transpose matrix) and established through the substitution $\theta_E \to -\theta_E$.

Appendix B: Auxiliary Integral F_0

The radial integral is solved by Taylor Expansion of the $\sinh t$, followed by the substitution $t^2 = s$ and integration over s with [11, 3.351.3]

$$\int_0^\infty e^{-s/k} s^n ds = n! k^{n+1}. \tag{B1}$$

$$\begin{aligned} F_0(k) \equiv \frac{1}{4k} e^{-k} \int_0^\infty dt e^{-t^2/(4k)} (e^t - e^{-t}) &= \frac{1}{4k} e^{-k} \int_0^\infty dt e^{-t^2/(4k)} 2 \sum_{l=1,3,5,\ldots} \frac{t^l}{l!} \\ &= \frac{1}{4k} e^{-k} \int_0^\infty ds e^{-s/(4k)} \sum_{l\geq 0} \frac{s^l}{(2l+1)!} \\ &= \frac{1}{4k} e^{-k} \sum_{l\geq 0} \frac{l!}{(2l+1)!} (4k)^{l+1} \\ &= e^{-k} \sum_{l\geq 0} \frac{[\Gamma(l+1)]^2}{\Gamma(2l+2)} \frac{(4k)^l}{l!}. \end{aligned} \tag{B2}$$

Application of the duplication formula for the Γ-function [12, 6.1.18] and rewriting the Γ-functions as Pochhammer symbols converts the series to a Confluent Hypergeometric Function [13, 14]:

$$F_0(k) = e^{-k}{}_1F_1(1;3/2;k) = {}_1F_1(1/2;3/2;-k) = \frac{1}{2}k^{-1/2}\lambda(1/2,k) = \frac{1}{2}k^{-1/2}\sqrt{\pi}\mathrm{erf}(\sqrt{k}). \tag{B3}$$

For small arguments [12, 7.1.5]

$$F_0(k) \stackrel{k\to 0}{\longrightarrow} 1 - \frac{1}{3}k + \frac{1}{10}k^2 - \frac{1}{42}k^3 + \frac{1}{108}k^4 + \cdots . \tag{B4}$$

Appendix C: Auxiliary Integral F_1

The auxiliary function introduced in (37) for real-valued argument $k \ge 0$ turns out to be closely related to the error function [15]. Very similar to the calculation in Appendix B, the exponentials in the integral that depend linearly on t are expanded in Taylor series [11, 1.212], summation and integration are interchanged, and integration via (B1) yields a Confluent Hypergeometric Series:

$$\begin{aligned}
F_1(k) = \frac{1}{4k}e^{-k}\int_0^\infty dt e^{-t^2/(4k)}\frac{1}{t^2}[e^{-t}(1+t)+e^t(t-1)] \\
= \frac{1}{4k}e^{-k}\int_0^\infty dt e^{-t^2/(4k)} 2\sum_{l\ge 0} t^{2l+1}\frac{2l+2}{(2l+3)!} \\
= \frac{1}{4k}e^{-k}\int_0^\infty ds e^{-s/(4k)} \sum_{l\ge 0} s^l\frac{2l+2}{(2l+3)!} \\
= \frac{1}{4k}e^{-k}\sum_{l\ge 0}(4k)^{l+1}\frac{(2l+2)l!}{(2l+3)!} \\
= 2e^{-k}\sum_{l\ge 0}\frac{(l+1)!l!}{(2l+3)!}\frac{(4k)^l}{l!} = \frac{1}{3}e^{-k}{}_1F_1(1;5/2;k).
\end{aligned} \tag{C1}$$

Kummer's transformation [11, 9.212] and a succession of well-known formulas for the Incomplete Gamma-function [12, 13.1.27,13.6.10,6.5.22] rephrase F_1 in terms of the error function:

$$F_1(k) = \frac{1}{3}{}_1F_1(3/2;5/2;-k) = \frac{1}{2}k^{-3/2}[\frac{\sqrt{\pi}}{2}\mathrm{erf}(\sqrt{k}) - \sqrt{k}e^{-k}]. \tag{C2}$$

For small arguments [12, 7.1.5]

$$F_1(k) \stackrel{k\to 0}{\longrightarrow} \frac{1}{3} - \frac{1}{5}k + \frac{1}{14}k^2 - \frac{1}{54}k^3 + \frac{1}{264}k^4 + \cdots . \tag{C3}$$

Appendix D: Shavitt's F-integral

F_0 and F_1 are special cases of Shavitt's F_ν-functions [16–21]

$$F_\nu(t) \equiv \int_0^1 u^{2\nu}e^{-tu^2}du = \frac{1}{2\nu+1}{}_1F_1(\nu+\frac{1}{2};\nu+\frac{3}{2};-t). \tag{D1}$$

Its first derivative is

$$\frac{d}{dt}F_\nu(t) = -F_{\nu+1}(t). \tag{D2}$$

The recurrence of the Confluent Hypergeometric Function [12, 13.4.7]

$$b(1-b+z){}_1F_1(a;b;z) + b(b-1){}_1F_1(a-1;b-1;z) - az{}_1F_1(a+1;b+1;z) = 0 \tag{D3}$$

establishes through insertion of $a = \nu + 3/2$, $b = \nu + 5/2$ the equivalent

$$zF_{\nu+2}(z) - (z + \nu + 3/2)F_{\nu+1}(z) + (\nu + 1/2)F_\nu(z) = 0 \tag{D4}$$

for F_ν. The Laplace transform is

$$\hat{F}_\nu(s) \equiv \int_0^\infty e^{-st} F_\nu(t) dt = \int_0^1 \frac{1}{s+u^2} du u^{2\nu}, \tag{D5}$$

$$\hat{F}_{\nu+1}(s) = \frac{1}{2\nu+1} - s\hat{F}_\nu(s), \tag{D6}$$

starting at

$$\hat{F}_0(s) = \int_0^1 \frac{1}{s+u^2} du = \frac{1}{\sqrt{s}} \arctan \frac{1}{\sqrt{s}}. \tag{D7}$$

The derivative with respect to the index is

$$\begin{aligned} \frac{d}{d\nu} F_\nu(t) = 2\int_0^1 \log u u^{2\nu} e^{-tu^2} du = 2\sum_{l\ge 0} \int_0^1 \log u u^{2\nu+2l} \frac{(-t)^l}{l!} du = -2\sum_{l\ge 0} \frac{(-t)^l}{l!} \frac{1}{(1+2\nu+2l)^2} \\ = -\frac{1}{2(1/2+\nu)^2} {}_2F_2\left(\begin{matrix} \nu+1/2, & \nu+1/2 \\ \nu+3/2, & \nu+3/2 \end{matrix} \mid -t \right). \end{aligned} \tag{D8}$$

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