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Integrals for non-Born–Oppenheimer calculations of molecules with three nuclei

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Variational molecular calculations without assuming the Born–Oppenheimer approximation of states corresponding to zero total angular momentum require the use of spherically symmetric basis functions explicitly depending on the electron–electron, electron–nucleus, and nucleus–nucleus distances. In our calculations, such functions have been the explicitly correlated Gaussians. For molecules with three nuclei, the Gaussians have to be multiplied by powers of all three internuclear distances to describe the highly correlated motion of the nuclei. In this work we have derived formulae for the overlap and the Hamiltonian matrix elements for such basis functions. Implementation of the formulae presents some unconventional numerical difficulties related to maintaining the required precision of the calculation. The implementation problems are discussed.

1. Introduction

Quantum mechanical (QM) molecular calculations without assuming the Born–Oppenheimer (BO) approximations regarding the separability of the motion of electrons (presumed fast) and the nuclear motion (presumed slow) are rare. There are several reasons contributing to low interest in such calculations. First of all, most problems that appear in chemistry concern molecular systems in ground electronic states at equilibrium geometries. For such systems the BO approximation works very well. Even if the system is electronically excited or it is distorted from equilibrium by vibrational motion, non-adiabatic effects rarely come into play, and, if they do, in most cases they can be treated using a local approach developed to describe conical intersections of the potential energy surfaces of two interacting electronic states. However, in order for the QM molecular calculations to match or predict gas-phase high-resolution spectroscopy results, especially for highly excited rho-vibrational states, one has to resort to calculations that invoke the BO approximation. For example, in our recent study of the HD^+ [1] system we showed quantitatively that, in the rotationless states lying near the dissociation limit, the electron is almost entirely localized around the deuteron. This purely non-adiabatic effect cannot be described with a method based on the BO approximation.

Another reason for the low popularity of non-BO calculations is their high degree of difficulty, resulting from the need to simultaneously describe both the electronic and the nuclear component of the wave function. The difficulty arises because not only do the electron–electron correlation effects have to be accurately described, but also the nucleus–nucleus correlation and the nucleus–electron correction have to be very well represented. One would think that since the electrons, as well as the nuclei, are particles with alike charges (and some nuclei such as protons are fermions as are the electrons) the electron correlation should be similar to the nucleus correlation. But this is not so, because, while the light electrons overlap significantly, the much heavier nuclei are separated from each other and overlap very little. The nucleus–electron correlation by itself represents a special class due to the attractive interaction, which causes the electrons (particularly the core electrons) to follow the nuclei. In order to accurately describe the three correlation effects mentioned above in the non-BO QM calculation, one needs to select a basis set that correctly describes the physical nature of the effects in the wave function. Basis set selection is the major challenge in such calculations.

Another aspect of basis set selection is related to the spatial symmetry of the non-adiabatic wave function that has to reflect the symmetry of the internal Hamiltonian operator that is obtained after the centre-of-mass motion is separated out. In our approach, the separation is accomplished by taking the full non-relativistic Hamiltonian expressed in terms of the

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laboratory Cartesian coordinates and by separating out the kinetic energy of the centre-of-mass motion. All particles in the system are treated as quantum particles. The total number of particles (i.e. the electrons and the nuclei) is set to be $n+1$ and their masses, charges and positions are denoted M_i, Q_i, and $\mathbf{R}_i$, respectively, where $i = 1, \ldots, n+1$. The laboratory frame non-relativistic Hamiltonian that includes the kinetic energy operator for each particle and the Coulombic interaction within each pair of particles has the form

$$\hat{H}_{\mathrm{TOT}} = -\sum_{i=1}^{n+1} \frac{1}{2M_i} \nabla_i^2 + \sum_{i=1}^{n+1} \sum_{j>i}^{n+1} \frac{Q_i Q_j}{R_{ij}}, \tag{1}$$

where $R_{ij} = |\mathbf{R}_j - \mathbf{R}_i|$ are the inter-particle distances. We then make a transformation to separate the centre-of-mass motion, thereby reducing the $(n+1)$-particle problem to an n-pseudoparticle problem described by the internal Hamiltonian, $\hat{H}$. In the new coordinate system, the first three coordinates are Cartesian coordinates of the position of the centre of mass of the system in the laboratory coordinate frame. The remaining $3n$ coordinates are coordinates describing the internal motion of the system. The internal coordinate system is obtained by placing a heavy particle at the origin of the system and by referring the other particles to that centre particle using the Cartesian position vectors $\mathbf{r}_i$ defined as $\mathbf{r}_i = \mathbf{R}_{i+1} - \mathbf{R}_1$. The resulting internal Hamiltonian is

$$\hat{H} = -\frac{1}{2}\left(\sum_{i}^{n} \frac{1}{\mu_i} \nabla_i^2 + \sum_{i \neq j}^{n} \frac{1}{M_1} \nabla_i' \nabla_j \right) + \sum_{i=1}^{n} \frac{q_0 q_i}{r_i} + \sum_{i<j}^{n} \frac{q_i q_j}{r_{ij}}. \tag{2}$$

This Hamiltonian describes a system containing the reference particle at the origin of the coordinates with charge $q_0 = Q_1$ and n pseudoparticles, or internal particles, which are characterized by the reduced masses $\mu_i = M_1 M_{i+1}/(M_1 + M_{i+1})$ and charges $q_i = Q_{i+1}$. The pseudoparticles are moving in the spherically symmetric potential generated by the reference particle placed at the origin of the internal coordinate system. The second term in parentheses is the mass polarization term that arises from the transformation of the laboratory frame coordinate system to the internal coordinate system, which couples the motion of all the particles. The potential energy terms r_i and r_{ij} are defined as $r_i = |\mathbf{r}_i|$ and $r_{ij} = |\mathbf{R}_{j+1} - \mathbf{R}_{i+1}| = |\mathbf{r}_j - \mathbf{r}_i|$. Due to its spherical symmetry, the internal Hamiltonian (2) resembles an atomic Hamiltonian. However, whereas in an atom, all particles moving in the central positive charge of the nucleus are only electrons, in the internal Hamiltonian (2) the pseudoparticles may have both positive and negative charges. Also, the mass of the pseudoparticles may be significantly larger than the mass of an electron.

The spherical symmetry (isotropy) of the internal Hamiltonian dictates that its eigenfunctions form an irreducible representation of a fully symmetric group of 3D rotations. In particular, the ground state of the molecule has to be fully symmetric with respect to all rotations. In our non-BO calculations of diatomic molecules with σ electrons we have used the following one-centre fully symmetric explicitly correlated Gaussian basis functions [1–6]:

$$\phi_k = r_1^{2m_k} \exp[-\mathbf{r}'(\mathbf{A}_k \otimes \mathbf{I}_3)\mathbf{r}], \tag{3}$$

where the matrix $\mathbf{A}_k$ is a symmetric matrix of exponential coefficients, $\mathbf{r}$ is a $3n \times 1$ vector of the internal Cartesian coordinates, $\mathbf{r}_i$, of the n pseudoparticles ($\mathbf{r}' = (\mathbf{r}_1', \mathbf{r}_2', \ldots, \mathbf{r}_n')$), $\mathbf{I}_3$ is the 3×3 identity matrix, and the pre-exponential multiplier is the internuclear distance, $\mathbf{r}_1$, raised to a non-negative even power $2m_k$. ϕ_k are rotationally invariant functions as required by the symmetry of the internal ground state of the Hamiltonian (2). The presence of $r_1^{2m_k}$ in (5) makes the function peak on a sphere centred at the origin. The radius of the sphere depends on the value of m_k and on the exponential parameters, $\mathbf{A}_k$. To describe a diatomic system, the maximum of ϕ_k in terms of r_1 should be around the equilibrium internuclear distance of the system. In the variational calculation, the maxima of ϕ_k are adjusted by optimization of m_k and $\mathbf{A}_k$. The explicit presence of the electron–electron, the nucleus–nucleus, and the nucleus–electron distances in the Gaussian exponent of ϕ_k, as well as the r_1 dependence of the pre-exponential multiplier, provides the necessary functional features for describing the three types of correlation effects mentioned above. It should be noted that due to the presence of the $r_1^{m_k}$ factor, the nucleus–nucleus correlation effects have a different functional representation in ϕ_k than the electron–electron correlation effects, since the $r_1^{m_k}$ factor significantly reduces nuclear overlapping.

In several recent papers [1–6], we have demonstrated that the explicitly correlated Gaussians (3) form a very effective basis set for non-BO calculations, not only for the ground state, but also for the 'vibrationally' excited states of diatomic systems. We put the term 'vibrational' in quotes because, in the non-BO approach, the vibrational and electronic degrees of freedom couple and cannot be separated. Thus, the 'vibrational states' in our calculations are states corresponding to a particular value of the total rotational quantum number. All our calculations so far have been performed for states with zero rotational quantum number.

The present work initiates the development of the non-BO approach for calculating the ground and excited states of triatomic molecules using a one-centre explicitly correlated Gaussian expansion for the wave function. We have already presented some non-BO calculations of molecular systems with more than three nuclei [8–10], but they were performed in the basis set of correlated Gaussians with shifted centres,

$$\phi_k = \exp[-(\mathbf{r}-\mathbf{s})'(\mathbf{A}_k \otimes \mathbf{I}_3)(\mathbf{r}-\mathbf{s})], \tag{4}$$

which are not spherically symmetric and do not allow direct separation of states corresponding to different rotational quantum numbers. The basis functions we consider in the present work are a direct extension of the one-centre explicitly correlated Gaussians used for the diatomic case (3). In order to accurately describe the correlated motion of the three nuclei in such a case, each basis function, in addition to containing the $r_1^{2n_k}$ pre-exponential factor, should also include similar factors involving the distances between nuclei 1 and 3, and 2 and 3, i.e. the factor $r_2^{2m_k} r_{12}^{2p_k}$. Such basis functions have the following form:

$$|\varphi_k\rangle = |r_1^{2n_k} r_2^{2m_k} r_{12}^{2p_k}\, \mathrm{e}^{-\mathbf{r}'(\mathbf{A}_k\otimes\mathbf{I}_3)\mathbf{r}}\rangle = |r_1^{2n_k} r_2^{2m_k} r_{12}^{2p_k}\phi_k\rangle, \tag{5}$$

where $\mathbf{A}_k$ is again a symmetric and positive definite matrix of exponential coefficients. As demonstrated in our application calculations for diatomic systems [1, 2, 6], large values of the powers of the internuclear distance, ranging from 0 to a few hundred, are needed to accurately describe the nucelus–nucleus correlation. Large and widespread powers are particularly important in calculations of higher excited vibrational states. This is not only due to the larger average internuclear distances in these states than in the ground state, but also due to the radial nodes in these states, the number of which increases with the level of excitation.

The aim of the present work was to derive formulae for the Hamiltonian matrix elements with basis functions (5). The task has been considerably more difficult than for diatomic integrals. As in the diatomic case, we have also used the powerful matrix differential calculus described by Kinghorn [7] to derive elegant and readily implementable mathematical forms of the integrals.

We begin the presentation by introducing the notation used throughout the paper and providing some basic information on the mathematical background. We then show the derivation of the integrals. In the last section we discuss the implementation of the formulae and the specific problems that are encountered in maintaining the accuracy of the calculations.

2. Mathematical background

Throughout this article we will use the following definitions, notation, and matrix properties.

2.1. *Definitions and notation*

The Pochhammer symbol is defined as

$$(a)_n = \prod_{k=0}^{n-1}(a+k) = \frac{\Gamma[a+n]}{\Gamma[a]}, \tag{6}$$

where $(a)_0 = 1$, and $\Gamma[x]$ is the Euler gamma function.

We will use the Leibniz formula to determine the Nth derivative of the product of functions f and g:

$$(f \circ g)^{(N)} = \sum_{k=0}^{N}\binom{N}{k} f^{(N-k)} g^{(k)}. \tag{7}$$

A matrix symbol with a *bar* over it ($\bar{\mathbf{A}}$) denotes the following Kronecker product:

$$\bar{\mathbf{A}} = \mathbf{A} \otimes \mathbf{I}_3,$$

where $\mathbf{I}_3$ is the 3×3 identity matrix.

The vec operator transforms a matrix into a vector by stacking the columns of the matrix to form a single vector and vec $\mathbf{ab}' = \mathbf{b} \otimes \mathbf{a}$.

The notation $[a(\ldots,i,j,k,l,\ldots)]_{j\times k}$, where $a(\ldots,i,j,k,l,\ldots)$ is a quantity depending on matrix elements with indices $\ldots,i,j,k,l,\ldots$, $i = 1,2,\ldots,I$, $j = 1,2,\ldots,J$, $k = 1,2,\ldots,K$ and $l = 1,2,\ldots,L$, defines the following $J \times K$ matrix:

$$[a(\ldots,i,j,k,l,\ldots)]_{j\times k} = \begin{bmatrix} a_{11}(\ldots,i,l,\ldots), & a_{12}(\ldots,i,l,\ldots), & \ldots, & a_{1K}(\ldots,i,l,\ldots) \\ a_{21}(\ldots,i,l,\ldots), & a_{22}(\ldots,i,l,\ldots), & \ldots, & a_{2K}(\ldots,i,l,\ldots) \\ \vdots & \vdots & \ddots & \vdots \\ a_{J1}(\ldots,i,l,\ldots), & a_{J2}(\ldots,i,l,\ldots), & \ldots, & a_{JK}(\ldots,i,l,\ldots) \end{bmatrix}. \tag{8}$$

Throughout this paper we will use the Einstein convection of summation:

$$a_i b^i = \sum_i a_i b_i.$$

2.2. *Matrix calculus*

In this section we list some matrix properties that will be used for evaluating the matrix elements of the overlap and Hamiltonian. Theorem 2.1 can be found in [7] and Theorem 2.2 has been taken from [11].

Theorem 2.1. *Let* $\mathbf{A}$ *and* $\mathbf{B}$ *be* $n \times n$ *matrices. Then*

$$|\mathbf{A} \otimes \mathbf{B}| = |\mathbf{A}|^n |\mathbf{B}|^n,$$
$$\mathrm{Tr}[\mathbf{A} \otimes \mathbf{B}] = \mathrm{Tr}[\mathbf{A}]\mathrm{Tr}[\mathbf{B}],$$
$$\mathrm{Tr}[\bar{\mathbf{A}}] = 3\mathrm{Tr}[\mathbf{A}],$$
$$\mathrm{Tr}[\mathbf{A}'\mathbf{B}] = (\mathrm{vec}\ \mathbf{A})'(\mathrm{vec}\ \mathbf{B}).$$

Theorem 2.2. *Let* $\mathbf{G}$ *and* $\mathbf{G}+\mathbf{H}$ *be non-singular matrices with* $\mathbf{H} = \sum_{i=1}^N \mathbf{H}_i$, $\mathbf{C}_1 = \mathbf{G}$, $\mathbf{C}_{i+1}^{-1} = \mathbf{C}_i^{-1} - \nu_i \mathbf{C}_i^{-1}\mathbf{H}_i\mathbf{C}_i^{-1}$ *and* $\nu_i^{-1} = 1 + \mathrm{Tr}[\mathbf{C}_i^{-1}\mathbf{H}_i]$, *and let* $\mathbf{H}_i$ *be a matrix of rank* 1. *Then*

$$|\mathbf{G} + H| = |\mathbf{G}| \prod_{i=1}^N \nu_i^{-1}.$$

Corollary 2.3. Let $\mathbf{G} = \mathbf{A}_{kl} + \alpha\mathbf{J}_{ii} + \beta\mathbf{J}_{jj} + \gamma\mathbf{J}_{ij}$ and

$$\mathbf{J}_{ij} = \begin{cases} \mathbf{E}_{ii}, & \text{if } i = j, \\ \mathbf{E}_{ii} + \mathbf{E}_{jj} - \mathbf{E}_{ij} - \mathbf{E}_{ji}, & \text{if } i \neq j, \end{cases}$$

where $\mathbf{E}_{ij}$ is the $n \times n$ matrix with 1 in its ijth position and 0 elsewhere. Then $|\mathbf{G}|(\alpha, \beta, \gamma)$ is linear in α, β and γ.

Proof. Using the Laplace theorem, one can expand $|\mathbf{G}|$ as a function of α, β and γ as

$$|\mathbf{G}| = \sum_{k=1}^n g_{\ell k}\mathbf{G}^\star_{\ell k},$$

where $\mathbf{G}^\star_{\ell k}$ is the cofactor of $g_{\ell k}$ defined by $G^\star_{\ell k} = (-1)^{\ell+k} M_{\ell k}$, $M_{\ell k}$ is the minor of matrix G, and $g_{\ell k}$ is a linear function of α, β or γ. □

Corollary 2.4. Let $\mathbf{G} = \mathbf{A} + \alpha\mathbf{J}_{ii} + \beta\mathbf{J}_{jj} + \gamma\mathbf{J}_{ij}$. Then

$$\frac{\partial^2|\mathbf{G}|}{\partial\gamma\partial\alpha} = \frac{\partial^2|\mathbf{G}|}{\partial\gamma\partial\beta}.$$

Proof. Corollary 2.3 implies that

$$\begin{aligned} \frac{\partial|\mathbf{G}|}{\partial\alpha} &= \frac{\partial}{\partial\alpha}\sum_k g_{\ell k}\mathbf{G}^\star_{\ell k} \\ &= \frac{\partial}{\partial\alpha}\sum_k (a_{\ell k} + \alpha\delta_{\ell k}\delta_{ki} + \beta\delta_{\ell k}\delta_{kj} + \gamma(\mathbf{J}_{ij})_{\ell k})\mathbf{G}^\star_{\ell k} \\ &= \sum_k \delta_{\ell k}\delta_{ki}\mathbf{G}^\star_{\ell k} = \delta_{\ell i}\mathbf{G}^\star_{\ell\ell}, \end{aligned} \tag{9}$$

$$\frac{\partial|\mathbf{G}|}{\partial\beta} = \delta_{\ell j}\mathbf{G}^\star_{\ell\ell}. \tag{10}$$

Then

$$\begin{aligned} \frac{\partial^2|\mathbf{G}|}{\partial\gamma\partial\alpha} &= \frac{\partial}{\partial\gamma}\delta_{\ell i}\mathbf{G}^\star_{\ell\ell} = \frac{\partial}{\partial\gamma}\sum_m \delta_{\ell i}(\mathbf{G}^\star_{\ell\ell})_{nm} \\ &\quad \times (\mathbf{G}^\star_{\ell\ell})^\star_{nm} = \delta_{\ell i}\delta_{nj}(\mathbf{G}^\star_{\ell\ell})^\star_{nn}, \end{aligned} \tag{11}$$

$$\begin{aligned} \frac{\partial^2|\mathbf{G}|}{\partial\gamma\partial\beta} &= \frac{\partial}{\partial\gamma}\delta_{\ell j}\mathbf{G}^\star_{\ell\ell} = \frac{\partial}{\partial\gamma}\sum_m \delta_{\ell j}(\mathbf{G}^\star_{\ell\ell})_{nm} \\ &\quad \times (\mathbf{G}^\star_{\ell\ell})^\star_{nm} = \delta_{\ell j}\delta_{ni}(\mathbf{G}^\star_{\ell\ell})^\star_{nn} \\ &= \delta_{\ell j}\delta_{ni}(\mathbf{G}^\star_{nn})^\star_{\ell\ell}. \end{aligned} \tag{12}$$

□

3. Hamiltonian in internal coordinates

The non-relativistic Hamiltonian (1) expressed in the laboratory Cartesian coordinates is transformed into the sum of the Hamiltonian describing the motion of the centre of mass and the internal Hamiltonian (2) by the following coordinate transformation $\hat{T}$ written here in matrix form ($\hat{T} : \mathbf{R} \longrightarrow [\mathbf{r}_0', \mathbf{r}']'$):

$$T = \begin{bmatrix} M_1/m_0 & M_2/m_0 & M_3/m_0 & \cdots & M_N/m_0 \\ -1 & 1 & 0 & \cdots & 0 \\ -1 & 0 & 1 & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ -1 & 0 & 0 & \cdots & 1 \end{bmatrix} \otimes \mathbf{I}_3, \tag{13}$$

where $m_0 = \sum_i^N M_i$, $\mathbf{r}_0$ is the coordinate of the centre of mass and $\mathbf{r}$ is a vector of internal coordinates, which has $3n = 3(N-1)$ elements. The internal Hamiltonian can be expressed in matrix form as

$$H = -\nabla_{\mathbf{r}}'(\mathbf{M} \otimes \mathbf{I}_3)\nabla_r + \sum_{i<j}^N \frac{q_i, q_j}{r_{ij}}, \tag{14}$$

where $\mathbf{M}$ is an $n \times n$ matrix with $1/\mu_i$ on the diagonal and $1/2M_1$ for off-diagonal elements, and μ_i is the reduced mass.

4. Basis set

The basis to be used in non-BO calculations of molecular systems with three nuclei was introduced in (5). To make the case more general, we consider in the derivations the basis functions in the following form (to obtain the basis functions (5) one needs to set $r_i = r_1$, $r_j = r_2$, and $r_{ij} = r_{12}$):

$$\begin{aligned} |\varphi_k\rangle &= |r_i^{2n_k} r_j^{2m_k} r_{ij}^{2p_k}\, \mathrm{e}^{-r'\bar{\mathbf{A}}_k r}\rangle \\ &= |r_i^{2n_k} r_j^{2m_k} r_{ij}^{2p_k}\phi_k\rangle, \end{aligned} \tag{15}$$

where $\bar{\mathbf{A}}_k$ is a symmetric and positive definite matrix of nonlinear variational parameters. r_i^{2n} can be expressed in the following form:

$$
\begin{aligned}
r_i^{2n} &= [\mathbf{r}'(\mathbf{J}_{ii}\otimes\mathbf{I}_3)\mathbf{r}]^n \\
&= (-1)^n \left.\frac{\partial^n \mathrm{e}^{-\alpha\mathbf{r}'\bar{J}_{ii}\mathbf{r}}}{\partial\alpha^n}\right|_{\alpha=0}.
\end{aligned} \tag{16}
$$

Expression (16) will be used to evaluate the matrix elements of the Hamiltonian and the overlap matrices.

5. Matrix elements

We start the evaluation of the Hamiltonian and overlap matrix elements with the evaluation of the following elemental integral (for details, see [5]):

$$
\begin{aligned}
\langle\phi_k \mid \phi_l\rangle &= \langle \mathrm{e}^{-\mathbf{r}'\bar{\mathbf{A}}_k\mathbf{r}} \mid \mathrm{e}^{-\mathbf{r}'\bar{\mathbf{A}}_l\mathbf{r}}\rangle \\
&= \int_0^\infty \mathrm{d}\mathbf{r}\,\mathrm{e}^{-\mathbf{r}\overbrace{(\bar{\mathbf{A}}_k+\bar{\mathbf{A}}_l)}^{\bar{\mathbf{A}}_{kl}}\mathbf{r}} \\
&= \pi^{3n/2}|\bar{\mathbf{A}}_{kl}|^{-1/2} = \pi^{3n/2}|\mathbf{A}_{kl}|^{-3/2} \\
&= \Gamma[1/2]^{3n}|\mathbf{A}_{kl}|^{-3/2}.
\end{aligned} \tag{17}
$$

5.1. *Overlap matrix element*

Taking into account that the basis function (15) can be expressed using derivatives of the exponential part of function (16), the overlap matrix element can be reduced to a product of derivatives of the elemental overlap integral (17),

$$
\begin{aligned}
S &= \langle\varphi_k \mid \varphi_l\rangle = \langle r_i^{2n_k} r_j^{2m_k} r_{ij}^{2p_k}\,\mathrm{e}^{-r'\bar{\mathbf{A}}_k r} \mid r_i^{2n_l} r_j^{2m_l} r_{ij}^{2p_l}\,\mathrm{e}^{-r'\bar{\mathbf{A}}_l r}\rangle \\
&= \left\langle \mathrm{e}^{-r'\bar{\mathbf{A}}_k r}\left| r_i^{2\overbrace{(n_k+n_l)}^{N}} r_j^{2\overbrace{(m_k+m_l)}^{M}} r_{ij}^{2\overbrace{(p_k+p_l)}^{P}}\right| \mathrm{e}^{-r'\bar{\mathbf{A}}_l r}\right\rangle \\
&= \left\langle\phi_k\left| r_i^{2N} r_j^{2M} r_{ij}^{2P}\right|\phi_l\right\rangle = (-1)^P\frac{\partial^P}{\partial\gamma^P}(-1)^M\frac{\partial^M}{\partial\beta^M}(-1)^N\frac{\partial^N}{\partial\alpha^N} \\
&\quad\times\left.\left\langle\phi_k\left|\mathrm{e}^{-\alpha\mathbf{r}'\bar{\mathbf{J}}_{ii}\mathbf{r}}\,\mathrm{e}^{-\beta\mathbf{r}'\bar{\mathbf{J}}_{jj}\mathbf{r}}\,\mathrm{e}^{-\gamma\mathbf{r}'\bar{\mathbf{J}}_{ij}\mathbf{r}}\right|\phi_l\right\rangle\right|_{\alpha=\beta=\gamma=0} \\
&= (-1)^P\frac{\partial^P}{\partial\gamma^P}(-1)^M\frac{\partial^M}{\partial\beta^M}(-1)^N\frac{\partial^N}{\partial\alpha^N} \\
&\quad\times\left.\int_{-\infty}^{\infty}\mathrm{d}\mathbf{r}\,\mathrm{e}^{-\mathbf{r}'\overbrace{(\bar{\mathbf{A}}_{kl}+\alpha\bar{\mathbf{J}}_{ii}+\beta\bar{\mathbf{J}}_{jj}+\gamma\bar{\mathbf{J}}_{ij})}^{\bar{\mathbf{G}}}\mathbf{r}}\right|_{\alpha=\beta=\gamma=0} \\
&= \Gamma[1/2]^{3n}(-1)^P\frac{\partial^P}{\partial\gamma^P}(-1)^M\frac{\partial^M}{\partial\beta^M}(-1)^N \\
&\quad\times\left.\frac{\partial^N}{\partial\alpha^N}|\mathbf{G}|^{-3/2}\right|_{\alpha=\beta=\gamma=0}.
\end{aligned} \tag{18}
$$

The last term in (18) has the form

$$
\begin{aligned}
\eta &= (-1)^N\frac{\partial^N|\mathbf{G}|^{-3/2}}{\partial\alpha^N} \\
&= \left(\frac{3}{2}\right)_N|\mathbf{G}|^{-3/2-N}\left(\frac{\partial|\mathbf{G}|}{\partial\alpha}\right)^N.
\end{aligned} \tag{19}
$$

Now, differentiating η with respect to β, recalling the Leibniz formula (7) and using Corollary 2.3 we obtain

$$
\begin{aligned}
\zeta &= (-1)^M\frac{\partial^M\eta}{\partial\beta^M} = (-1)^M\left(\frac{3}{2}\right)_N\frac{\partial^M|\mathbf{G}|^{-3/2-N}(\partial|\mathbf{G}|/\partial\alpha)^N}{\partial\beta^M} \\
&= (-1)^M\left(\frac{3}{2}\right)_N\sum_k^M\binom{M}{k}\frac{\partial^{M-k}|\mathbf{G}|^{-3/2-N}}{\partial\beta^{M-k}}\frac{\partial^k(\partial|\mathbf{G}|/\partial\alpha)^N}{\partial\beta^k} \\
&= (-1)^M\left(\frac{3}{2}\right)_N\sum_k^M\binom{M}{k}(-1)^{M-k}\left(\frac{3}{2}+N\right)_{M-k}\frac{N!}{(N-k)!} \\
&\quad\times|\mathbf{G}|^{-3/2-N-M+k}\left(\frac{\partial|\mathbf{G}|}{\partial\beta}\right)^{M-k}\left(\frac{\partial|\mathbf{G}|}{\partial\alpha}\right)^{N-k}\left(\frac{\partial^2|\mathbf{G}|}{\partial\beta\,\partial\alpha}\right)^k \\
&= \frac{N!}{\Gamma[3/2]}\sum_k^M\binom{M}{k}(-1)^{-k} \\
&\quad\times\frac{\Gamma[3/2+N+M-k](\partial^2|\mathbf{G}|/\partial\beta\,\partial\alpha)^k}{(N-k)!} \\
&\quad\times|\mathbf{G}|^{-3/2-N-M+k}\left(\frac{\partial|\mathbf{G}|}{\partial\beta}\right)^{M-k}\left(\frac{\partial|\mathbf{G}|}{\partial\alpha}\right)^{N-k}.
\end{aligned} \tag{20}
$$

Finally, we need to calculate the Pth derivative of (20)

$$
\begin{aligned}
\xi &= (-1)^P\frac{\partial^P\zeta}{\partial\gamma^P} = (-1)^P\frac{N!}{\Gamma[3/2]}\sum_k^M\binom{M}{k} \\
&\quad\times\frac{(-1)^{-k}\Gamma[3/2+N+M-k](\partial^2|\mathbf{G}|/\partial\beta\,\partial\alpha)^k}{(N-k)!} \\
&\quad\times\frac{\partial^P|\mathbf{G}|^{-3/2-N-M+k}(\partial|\mathbf{G}|/\partial\beta)^{M-k}(\partial|\mathbf{G}|/\partial\alpha)^{N-k}}{\partial\gamma^P} \\
&= (-1)^P\frac{N!}{\Gamma[3/2]}\sum_k^M\binom{M}{k} \\
&\quad\times\frac{(-1)^{-k}\Gamma[3/2+N+M-k](\partial^2|\mathbf{G}|/\partial\beta\,\partial\alpha)^k}{(N-k)!} \\
&\quad\times\sum_{\ell=0}^P\binom{P}{\ell}\frac{\partial^{P-\ell}|\mathbf{G}|^{-3/2-N-M+k}}{\partial\gamma^{P-\ell}} \\
&\quad\times\sum_{m=0}^{\ell}\binom{\ell}{m}\frac{\partial^{\ell-m}(\partial|\mathbf{G}|/\partial\beta)^{M-k}}{\partial\gamma^{\ell-m}}\frac{\partial^m(\partial|\mathbf{G}|/\partial\alpha)^{N-k}}{\partial\gamma^m}
\end{aligned}
$$

$$
\begin{aligned}
&= (-1)^P \frac{N!}{\Gamma[3/2]} \sum_k^M \binom{M}{k} \\
&\quad \times \frac{(-1)^{-k}\Gamma[3/2+N+M-k](\partial^2|\mathbf{G}|/\partial\beta\,\partial\alpha)^k}{(N-k)!} \\
&\quad \times \sum_{\ell=0}^{P} \binom{P}{\ell} \left(\frac{3}{2}+N+M-k\right)_{P-\ell} \\
&\quad \times (-1)^{P-\ell} |\mathbf{G}|^{-3/2-N-M+k-P+\ell} \\
&\quad \times \left(\frac{\partial|\mathbf{G}|}{\partial\gamma}\right)^{P-\ell} \sum_{m=0}^{\ell} \binom{\ell}{m} \times (M-k-\ell+m+1)_{\ell-m} \\
&\quad \times \left(\frac{\partial|\mathbf{G}|}{\partial\beta}\right)^{M-k-\ell+m} \left(\frac{\partial^2|\mathbf{G}|}{\partial\gamma\,\partial\beta}\right)^{\ell-m} \\
&\quad \times (N-k-m+1)_m \left(\frac{\partial|\mathbf{G}|}{\partial\alpha}\right)^{N-k-m} \left(\frac{\partial^2|\mathbf{G}|}{\partial\gamma\,\partial\alpha}\right)^{m} \\
&= \frac{N!M!P!}{\Gamma[3/2]\sqrt{|\mathbf{G}|^3}} \left(\frac{(\partial|\mathbf{G}|/\partial\alpha)}{|\mathbf{G}|}\right)^N \left(\frac{(\partial|\mathbf{G}|/\partial\beta)}{|\mathbf{G}|}\right)^M \\
&\quad \times \left(\frac{(\partial|\mathbf{G}|/\partial\gamma)}{|\mathbf{G}|}\right)^P \sum_k^M \frac{1}{k!} \left(\frac{-|\mathbf{G}|(\partial^2|\mathbf{G}|/\partial\beta\,\partial\alpha)}{(\partial|\mathbf{G}|/\partial\beta)(\partial|\mathbf{G}|/\partial\alpha)}\right)^k \\
&\quad \times \sum_{\ell=0}^{P} \frac{\Gamma[N+M+P+3/2-k-\ell]}{(P-\ell)!} \\
&\quad \times \left(\frac{-|\mathbf{G}|(\partial^2|\mathbf{G}|/\partial\gamma\,\partial\beta)}{(\partial|\mathbf{G}|/\partial\beta)(\partial|\mathbf{G}|/\partial\gamma)}\right)^\ell \sum_{m=0}^{\ell} \frac{1}{m!(\ell-m)!} \\
&\quad \times \frac{1}{(M-k-\ell+m)!(N-k-m)!} \\
&\quad \times \left(\frac{(\partial|\mathbf{G}|/\partial\beta)(\partial^2|\mathbf{G}|/\partial\gamma\,\partial\alpha)}{(\partial|\mathbf{G}|/\partial\alpha)(\partial^2|\mathbf{G}|/\partial\gamma\,\partial\beta)}\right)^m .
\end{aligned} \tag{21}
$$

Then, after substituting (21) into (18), the overlap matrix element is given by

$$
\begin{aligned}
S &= \frac{2\Gamma[1/2]^{3n-1}N!M!P!}{\sqrt{|\mathbf{G}|^3}} \left(\frac{(\partial|\mathbf{G}|/\partial\alpha)}{|\mathbf{G}|}\right)^N \left(\frac{(\partial|\mathbf{G}|/\partial\beta)}{|\mathbf{G}|}\right)^M \\
&\quad \times \left(\frac{(\partial|\mathbf{G}|/\partial\gamma)}{|\mathbf{G}|}\right)^P \sum_k^M \frac{1}{k!} \left(\frac{-|\mathbf{G}|(\partial^2|\mathbf{G}|/\partial\beta\,\partial\alpha)}{(\partial|\mathbf{G}|/\partial\beta)(\partial|\mathbf{G}|/\partial\alpha)}\right)^k \\
&\quad \times \sum_{\ell=0}^{P} \frac{\Gamma[N+M+P+3/2-k-\ell]}{(P-\ell)!} \\
&\quad \times \left(\frac{-|\mathbf{G}|(\partial^2|\mathbf{G}|/\partial\gamma\,\partial\beta)}{(\partial|\mathbf{G}|/\partial\beta)(\partial|\mathbf{G}|/\partial\gamma)}\right)^\ell \\
&\quad \times \sum_{m=0}^{\ell} \frac{1}{m!(\ell-m)!(M-k-\ell+m)!(N-k-m)!} \\
&\quad \times \left(\frac{(\partial|\mathbf{G}|/\partial\beta)}{(\partial|\mathbf{G}|/\partial\alpha)}\right)^m \Bigg|_{\alpha=\beta=\gamma=0},
\end{aligned} \tag{22}
$$

where the first and second derivatives of $|\mathbf{G}|$ will be explicitly shown in section 5.3.

5.2. *Coulomb matrix elements*

Using the integral representation of r_{st}^{-1},

$$
r_{st}^{-1} = \frac{2}{\sqrt{\pi}} \int_0^\infty \mathrm{d}x\, \mathrm{e}^{-x^2 r' \bar{J}_{st} r}, \tag{23}
$$

and recalling formulae (16) and (17), one readily finds that the potential energy matrix element can be expressed as

$$
\begin{aligned}
V &= \langle \varphi_k | r_{st}^{-1} | \varphi_l \rangle \\
&= \Gamma[1/2]^{3n}(-1)^P \frac{\partial^P}{\partial\gamma^P}(-1)^M \frac{\partial^M}{\partial\beta^M}(-1)^N \\
&\quad \times \frac{\partial^N}{\partial\alpha^N} \frac{2}{\sqrt{\pi}} \int_0^\infty |\mathbf{D}|^{-3/2}\, \mathrm{d}x \Bigg|_{\alpha=\beta=\gamma=0},
\end{aligned} \tag{24}
$$

where $M = m_k + m_l$, $N = n_k + n_l$, $P = p_k + p_l$ and

$$
\begin{aligned}
|\mathbf{D}| &= \Big| \overbrace{\mathbf{A}_{kl} + \alpha\mathbf{J}_{ii} + \beta\mathbf{J}_{jk} + \gamma\mathbf{J}_{ij}}^{\mathbf{G}} + x^2\mathbf{J}_{st} \Big| \\
&= |\mathbf{G} + x^2\mathbf{J}_{st}|.
\end{aligned}
$$

Integration over x in the last term of (24) yields

$$
\begin{aligned}
\kappa &= \int_0^\infty \mathrm{d}x\, |\mathbf{D}|^{-3/2} \\
&= |\mathbf{G}|^{-3/2} \int_0^\infty \mathrm{d}x\, (1 + x^2 \mathrm{Tr}[\mathbf{G}\mathbf{J}_{st}])^{-3/2} \\
&= |\mathbf{G}|^{-3/2} \mathrm{Tr}^{-1/2}[\mathbf{G}^{-1}\mathbf{J}_{st}].
\end{aligned} \tag{25}
$$

Now, since $\mathbf{J}_{st}$ has rank one, we can use Theorem 2.2 and rewrite (25) as follows:

$$
\begin{aligned}
\kappa &= |\mathbf{G}|^{-1}(|\mathbf{G}|(1 + \mathrm{Tr}[\mathbf{G}^{-1}\mathbf{J}_{st}]) - |\mathbf{G}|)^{-1/2} \\
&= |\mathbf{G}|^{-1}(|\mathbf{F}| - |\mathbf{G}|)^{-1/2},
\end{aligned} \tag{26}
$$

where $|\mathbf{F}| = |\mathbf{G} + \mathbf{J}_{st}|$ is a linear function of α, β and γ.

Differentiating (26) with respect to α, applying the Leibniz formula (7) and using Corollaries 2.3 and 2.4 we obtain

$$
\begin{aligned}
\eta &= (-1)^N \frac{\partial^N \kappa}{\partial\alpha^N} = (-1)^N \sum_{k=0}^{N} \binom{N}{k} \frac{\partial^{N-k}|\mathbf{G}|^{-1}}{\partial\alpha^{N-k}} \frac{\partial^k(|\mathbf{F}|-|\mathbf{G}|)^{-1/2}}{\partial\alpha^k} \\
&= (-1)^N \sum_{k=0}^{N} \binom{N}{k} (-1)^{N-k}(1)_{N-k} |\mathbf{G}|^{-1-N+k} \left(\frac{\partial|\mathbf{G}|}{\partial\alpha}\right)^{N-k} \\
&\quad \times (-1)^k \left(\frac{1}{2}\right)_k (|\mathbf{F}|-|\mathbf{G}|)^{-1/2-k} \left(\frac{\partial|\mathbf{F}|}{\partial\alpha} - \frac{\partial|\mathbf{G}|}{\partial\alpha}\right)^k
\end{aligned}
$$

$$= \sum_{k=0}^{N} \binom{N}{k} (1)_{N-k} \left(\frac{1}{2}\right)_k |\mathbf{G}|^{-1-N+k} \left(\frac{\partial |\mathbf{G}|}{\partial \alpha}\right)^{N-k} \times (|\mathbf{F}| - |\mathbf{G}|)^{-1/2-k} \left(\frac{\partial |\mathbf{F}|}{\partial \alpha} - \frac{\partial |\mathbf{G}|}{\partial \alpha}\right)^k. \qquad (27)$$

Differentiation of (27) with respect to β gives

$$\begin{aligned}
\zeta &= (-1)^M \frac{\partial^M \eta}{\partial \beta^M} = (-1)^M \sum_{k=0}^{N} \binom{N}{k} (1)_{N-k} \left(\frac{1}{2}\right)_k \sum_{\ell=0}^{M} \binom{M}{\ell} \\
&\quad \times \frac{\partial^{M-\ell} |\mathbf{G}|^{-1-N+k} (\partial |\mathbf{G}|/\partial \alpha)^{N-k}}{\partial \beta^{M-\ell}} \\
&\quad \times \frac{\partial^{\ell} (|\mathbf{F}| - |\mathbf{G}|)^{-1/2-k} ((\partial |\mathbf{F}|/\partial \alpha) - (\partial |\mathbf{G}|/\partial \alpha))^k}{\partial \beta^{\ell}} \\
&= (-1)^M \sum_{k=0}^{N} \binom{N}{k} (1)_{N-k} (1/2)_k \sum_{\ell=0}^{M} \binom{M}{\ell} \sum_{s=0}^{M-\ell} \binom{M-\ell}{s} \\
&\quad \times \frac{\partial^{M-\ell-s} |\mathbf{G}|^{-1-N+k}}{\partial \beta^{M-\ell-s}} \frac{\partial^{s} (\partial |\mathbf{G}|/\partial \alpha)^{N-k}}{\partial \beta^{s}} \\
&\quad \times \sum_{t=0}^{\ell} \binom{\ell}{t} \frac{\partial^{\ell-t} ((\partial |\mathbf{F}|/\partial \alpha) - (\partial |\mathbf{G}|/\partial \alpha))^k}{\partial \beta^{\ell-t}} \\
&\quad \times \frac{\partial^{t} (|\mathbf{F}| - |\mathbf{G}|)^{-1/2-k}}{\partial \beta^{t}} \\
&= (-1)^M \sum_{k=0}^{N} \binom{N}{k} (1)_{N-k} \left(\frac{1}{2}\right)_k \sum_{\ell=0}^{M} \binom{M}{\ell} \sum_{s=0}^{M-\ell} \binom{M-\ell}{s} \\
&\quad \times (-1)^{M-\ell-s} (N+1-k)_{M-\ell-s} \\
&\quad \times |\mathbf{G}|^{-1-N+k-M+\ell+s} \left(\frac{\partial |\mathbf{G}|}{\partial \beta}\right)^{M-\ell-s} \\
&\quad \times (N-k-s+1)_s \left(\frac{\partial |\mathbf{G}|}{\partial \alpha}\right)^{N-k-s} \left(\frac{\partial^2 |\mathbf{G}|}{\partial \beta\, \partial \alpha}\right)^{s} \\
&\quad \times \sum_{t=0}^{\ell} \binom{\ell}{t} (k-\ell+t+1)_{\ell-t} \\
&\quad \times \left(\frac{\partial |\mathbf{F}|}{\partial \alpha} - \frac{\partial |\mathbf{G}|}{\partial \alpha}\right)^{k-\ell+t} \left(\frac{\partial^2 |\mathbf{F}|}{\partial \gamma \partial \alpha} - \frac{\partial^2 |\mathbf{G}|}{\partial \gamma \partial \alpha}\right)^{\ell-t} \\
&\quad \times (-1)^t \left(\frac{1}{2}+k\right)_t \\
&\quad \times (|\mathbf{F}| - |\mathbf{G}|)^{-(1/2)-k-t} \left(\frac{\partial |\mathbf{F}|}{\partial \beta} - \frac{\partial |\mathbf{G}|}{\partial \beta}\right)^{t} \\
&= \frac{N!}{\Gamma[1/2]} \sum_{k=0}^{N} \sum_{\ell=0}^{M} \binom{M}{\ell} (-1)^{\ell} \sum_{s=0}^{M-\ell} \binom{M-\ell}{s} (-1)^{-s} \\
&\quad \times \frac{\Gamma[N+M+1-k-\ell-s] (\partial^2 |\mathbf{G}|/\partial \beta\, \partial \alpha)^s}{\Gamma[N-k-s+1]} \\
&\quad \times |\mathbf{G}|^{-1-N+k-M+\ell+s} \left(\frac{\partial |\mathbf{G}|}{\partial \beta}\right)^{M-\ell-s} \\
&\quad \times \left(\frac{\partial |\mathbf{G}|}{\partial \alpha}\right)^{N-k-s} \sum_{t=0}^{\ell} \binom{\ell}{t} (-1)^t \\
&\quad \times \frac{\Gamma[1/2+k+t] ((\partial^2 |\mathbf{F}|/\partial \beta\, \partial \alpha) - (\partial^2 |\mathbf{G}|/\partial \beta\, \partial \alpha))^{\ell-t}}{\Gamma[k-\ell+t+1]} \\
&\quad \times \left(\frac{\partial |\mathbf{F}|}{\partial \alpha} - \frac{\partial |\mathbf{G}|}{\partial \alpha}\right)^{k-\ell+t} (|\mathbf{F}| - |\mathbf{G}|)^{-1/2-k-t} \\
&\quad \times \left(\frac{\partial |\mathbf{F}|}{\partial \beta} - \frac{\partial |\mathbf{G}|}{\partial \beta}\right)^{t}.
\end{aligned} \qquad (28)$$

Then, differentiating (28) with respect to γ and simplifying gives the result

$$\begin{aligned}
\xi &= (-1)^P \frac{\partial^P \zeta}{\partial \gamma^P} = \frac{(-1)^P N!}{\Gamma[1/2]} \sum_{k=0}^{N} \sum_{\ell=0}^{M} \binom{M}{\ell} (-1)^{\ell} \sum_{s=0}^{M-\ell} \binom{M-\ell}{s} \\
&\quad \times \frac{(-1)^{-s} \Gamma[N+M+1-k-\ell-s] (\partial^2 |\mathbf{G}|/\partial \beta\, \partial \alpha)^s}{\Gamma[N-k-s+1]} \\
&\quad \times \sum_{m=0}^{P} \binom{P}{m} \frac{\partial^{P-m} \left(\begin{aligned} &|\mathbf{G}|^{-1-N+k-M+\ell+s} \\ &\times (\partial |\mathbf{G}|/\partial \beta)^{M-\ell-s} (\partial |\mathbf{G}|/\partial \alpha)^{N-k-s} \end{aligned} \right)}{\partial \gamma^{P-m}} \\
&\quad \times \sum_{t=0}^{\ell} \binom{\ell}{t} \frac{\left(\begin{aligned} &(-1)^t \Gamma[1/2+k+t] \\ &\times ((\partial^2 |\mathbf{F}|/\partial \beta\, \partial \alpha) - (\partial^2 |\mathbf{G}|/\partial \beta\, \partial \alpha))^{\ell-t} \end{aligned} \right)}{\Gamma[k-\ell+t+1]} \\
&\quad \times \frac{\partial^m \left(\begin{aligned} &((\partial |\mathbf{F}|/\partial \alpha) - (\partial |\mathbf{G}|/\partial \alpha))^{k-\ell+t} \\ &\times (|\mathbf{F}| - |\mathbf{G}|)^{-1/2-k-t} ((\partial |\mathbf{F}|/\partial \beta) - (\partial |\mathbf{G}|/\partial \beta))^t \end{aligned} \right)}{\partial \gamma^m} \\
&= \frac{(-1)^P N!}{\Gamma[1/2]} \sum_{k=0}^{N} \sum_{\ell=0}^{M} \binom{M}{\ell} (-1)^{\ell} \sum_{s=0}^{M-\ell} \binom{M-\ell}{s} \\
&\quad \times \frac{(-1)^{-s} \Gamma[N+M+1-k-\ell-s] (\partial^2 |\mathbf{G}|/\partial \beta\, \partial \alpha)^s}{\Gamma[N-k-s+1]} \\
&\quad \times \sum_{m=0}^{P} \binom{P}{m} \sum_{a=0}^{P-m} \binom{P-m}{a} \frac{\partial^{P-m-a} |\mathbf{G}|^{-1-N+k-M+\ell+s}}{\partial \gamma^{P-m-a}} \\
&\quad \times \sum_{b=0}^{a} \binom{a}{b} \frac{\partial^{a-b} (\partial |\mathbf{G}|/\partial \beta)^{M-\ell-s}}{\partial \gamma^{a-b}} \frac{\partial^{b} (\partial |\mathbf{G}|/\partial \alpha)^{N-k-s}}{\partial \gamma^{b}} \\
&\quad \times \sum_{t=0}^{\ell} \binom{\ell}{t} \frac{\left(\begin{aligned} &(-1)^t \Gamma[1/2+k+t] \\ &\times ((\partial^2 |\mathbf{F}|/\partial \beta\, \partial \alpha) - (\partial^2 |\mathbf{G}|/\partial \beta\, \partial \alpha))^{\ell-t} \end{aligned} \right)}{\Gamma[k-\ell+t+1]}
\end{aligned}$$

$$\times\sum_{c=0}^{m}\binom{m}{c}\frac{\partial^{m-c}((\partial|\mathbf{F}|/\partial\alpha)-(\partial|\mathbf{G}|/\partial\alpha))^{k-\ell+t}}{\partial\gamma^{m-c}}\sum_{d=0}^{c}\binom{c}{d}$$
$$\times\frac{\partial^{c-d}(|\mathbf{F}|-|\mathbf{G}|)^{-1/2-k-t}}{\partial\gamma^{c-d}}\frac{\partial^{d}((\partial|\mathbf{F}|/\partial\beta)-(\partial|\mathbf{G}|/\partial\beta))^{t}}{\partial\gamma^{d}}$$
$$=\frac{(-1)^{P}N!}{\Gamma[1/2]}\sum_{k=0}^{N}\sum_{\ell=0}^{M}\binom{M}{\ell}(-1)^{\ell}\sum_{s=0}^{M-\ell}\binom{M-\ell}{s}$$
$$\times\frac{(-1)^{-s}\Gamma[N+M+1-k-\ell-s](\partial^2|\mathbf{G}|/\partial\beta\,\partial\alpha)^{s}}{\Gamma[N-k-s+1]}$$
$$\times\sum_{m=0}^{P}\binom{P}{m}\sum_{a=0}^{P-m}\binom{P-m}{a}(-1)^{P-m-a}$$
$$\times(N+M+1-k-\ell-s)_{P-m-a}$$
$$\times|\mathbf{G}|^{-1-N-M+k+\ell+s-P+m+a}\left(\frac{\partial|\mathbf{G}|}{\partial\gamma}\right)^{P-m-a}$$
$$\times\sum_{b=0}^{a}\binom{a}{b}(M-\ell-s-a+b+1)_{a-b}$$
$$\times\left(\frac{\partial|\mathbf{G}|}{\partial\beta}\right)^{M-\ell-s-a+b}\left(\frac{\partial^2|\mathbf{G}|}{\partial\gamma\,\partial\beta}\right)^{a-b}(N-k-s-b+1)_{b}$$
$$\times\left(\frac{\partial|\mathbf{G}|}{\partial\alpha}\right)^{N-k-s-b}\left(\frac{\partial^2|\mathbf{G}|}{\partial\gamma\,\partial\alpha}\right)^{b}$$
$$\times\sum_{t=0}^{\ell}\binom{\ell}{t}\frac{\left(\begin{array}{c}(-1)^{t}\Gamma[1/2+k+t]\\ ((\partial^2|\mathbf{F}|/\partial\beta\,\partial\alpha)-(\partial^2|\mathbf{G}|/\partial\beta\,\partial\alpha))^{\ell-t}\end{array}\right)}{\Gamma[k-\ell+t+1]}$$
$$\times\sum_{c=0}^{m}\binom{m}{c}(k-\ell+t-m+c)_{m-c}\left(\frac{\partial|\mathbf{F}|}{\partial\alpha}-\frac{\partial|\mathbf{G}|}{\partial\alpha}\right)^{k-\ell+t-m+c}$$
$$\times\left(\frac{\partial^2|\mathbf{F}|}{\partial\gamma\partial\alpha}-\frac{\partial^2|\mathbf{G}|}{\partial\gamma\partial\alpha}\right)^{m-c}$$
$$\times\sum_{d=0}^{c}\binom{c}{d}(-1)^{c-d}(1/2+k+t)_{c-d}(|\mathbf{F}|-|\mathbf{G}|)^{-1/2-k-t-c+d}$$
$$\times\left(\frac{\partial|\mathbf{F}|}{\partial\gamma}-\frac{\partial|\mathbf{G}|}{\partial\gamma}\right)^{c-d}$$
$$\times\frac{t!}{(t-d)!}\left(\frac{\partial|\mathbf{F}|}{\partial\beta}-\frac{\partial|\mathbf{G}|}{\partial\beta}\right)^{t-d}\left(\frac{\partial^2|\mathbf{F}|}{\partial\gamma\partial\beta}-\frac{\partial^2|\mathbf{G}|}{\partial\gamma\partial\beta}\right)^{d}$$
$$=\frac{N!}{\Gamma[1/2]|\mathbf{G}|\sqrt{|\mathbf{F}|-|\mathbf{G}|}}\left(\frac{(\partial|\mathbf{G}|/\partial\alpha)}{|\mathbf{G}|}\right)^{N}\left(\frac{(\partial|\mathbf{G}|/\partial\beta)}{|\mathbf{G}|}\right)^{M}$$
$$\times\left(\frac{(\partial|\mathbf{G}|/\partial\gamma)}{|\mathbf{G}|}\right)^{P}\sum_{k=0}^{N}\left(\frac{|\mathbf{G}|((\partial|\mathbf{F}|/\partial\alpha)-(\partial|\mathbf{G}|/\partial\alpha))}{(|\mathbf{F}|-|\mathbf{G}|)(\partial|\mathbf{G}|/\partial\alpha)}\right)^{k}$$
$$\times\sum_{\ell=0}^{M}\binom{M}{\ell}\left(\frac{-|\mathbf{G}|\big((\partial^2|\mathbf{F}|/\partial\beta\,\partial\alpha)-(\partial^2|\mathbf{G}|/\partial\beta\,\partial\alpha)\big)}{(\partial|\mathbf{G}|/\partial\beta)((\partial|\mathbf{F}|/\partial\alpha)-(\partial|\mathbf{G}|/\partial\alpha))}\right)^{\ell}$$
$$\times\sum_{s=0}^{M-\ell}\binom{M-\ell}{s}\left(\frac{-|\mathbf{G}|(\partial^2|\mathbf{G}|/\partial\beta\,\partial\alpha)}{(\partial|\mathbf{G}|/\partial\beta)(\partial|\mathbf{G}|/\partial\alpha)}\right)^{s}$$
$$\times\sum_{m=0}^{P}\binom{P}{m}\left(\frac{-|\mathbf{G}|\big((\partial^2|\mathbf{F}|/\partial\gamma\,\partial\alpha)-(\partial^2|\mathbf{G}|/\partial\gamma\,\partial\alpha)\big)}{(\partial|\mathbf{G}|/\partial\gamma)((\partial|\mathbf{F}|/\partial\alpha)-(\partial|\mathbf{G}|/\partial\alpha))}\right)^{m}$$
$$\times\sum_{a=0}^{P-m}\binom{P-m}{a}\Gamma[N+M+1-k-\ell-s+P-m-a]$$
$$\times\left(\frac{-|\mathbf{G}|(\partial^2|\mathbf{G}|/\partial\gamma\,\partial\beta)}{(\partial|\mathbf{G}|/\partial\gamma)(\partial|\mathbf{G}|/\partial\beta)}\right)^{a}$$
$$\times\sum_{b=0}^{a}\binom{a}{b}\frac{\Gamma[M-\ell-s+1]}{\Gamma[M-\ell-s-a+b+1]\Gamma[N-k-s-b+1]}$$
$$\times\left(\frac{(\partial|\mathbf{G}|/\partial\beta)(\partial^2|\mathbf{G}|/\partial\gamma\,\partial\alpha)}{(\partial|\mathbf{G}|/\partial\alpha)(\partial^2|\mathbf{G}|/\partial\gamma\,\partial\beta)}\right)^{b}\sum_{t=0}^{\ell}\binom{\ell}{t}\frac{t!}{k-\ell+t}$$
$$\times\left(\frac{-((\partial|\mathbf{F}|/\partial\beta)-(\partial|\mathbf{G}|/\partial\beta))((\partial|\mathbf{F}|/\partial\alpha)-(\partial|\mathbf{G}|/\partial\alpha))}{(|\mathbf{F}|-|\mathbf{G}|)((\partial^2|\mathbf{F}|/\partial\beta\,\partial\alpha)-(\partial^2|\mathbf{G}|/\partial\beta\,\partial\alpha))}\right)^{t}$$
$$\times\sum_{c=0}^{m}\binom{m}{c}\frac{1}{\Gamma[k-\ell+t-m+c]}$$
$$\times\left(\frac{-((\partial|\mathbf{F}|/\partial\gamma)-(\partial|\mathbf{G}|/\partial\gamma))((\partial|\mathbf{F}|/\partial\alpha)-(\partial|\mathbf{G}|/\partial\alpha))}{(|\mathbf{F}|-|\mathbf{G}|)((\partial^2|\mathbf{F}|/\partial\gamma\,\partial\alpha)-(\partial^2|\mathbf{G}|/\partial\gamma\,\partial\alpha))}\right)^{c}$$
$$\times\sum_{d=0}^{c}\binom{c}{d}\frac{\Gamma[1/2+k+t+c-d]}{(t-d)!}$$
$$\times\left(\frac{-(|\mathbf{F}|-|\mathbf{G}|)((\partial^2|\mathbf{F}|/\partial\gamma\,\partial\beta)-(\partial^2|\mathbf{G}|/\partial\gamma\,\partial\beta))}{((\partial|\mathbf{F}|/\partial\gamma)-(\partial|\mathbf{G}|/\partial\gamma))((\partial|\mathbf{F}|/\partial\beta)-(\partial|\mathbf{G}|/\partial\beta))}\right)^{d}. \qquad (29)$$

Finally, substituting (29) into (27) and simplifying the result we get

$$V=\frac{4\Gamma[1/2]^{3n-2}N!}{|\mathbf{G}|\sqrt{|\mathbf{F}|-|\mathbf{G}|}}\left(\frac{(\partial|\mathbf{G}|/\partial\alpha)}{|\mathbf{G}|}\right)^{N}\left(\frac{(\partial|\mathbf{G}|/\partial\beta)}{|\mathbf{G}|}\right)^{M}$$
$$\times\left(\frac{(\partial|\mathbf{G}|/\partial\gamma)}{|\mathbf{G}|}\right)^{P}\sum_{k=0}^{N}\left(\frac{|\mathbf{G}|((\partial|\mathbf{F}|/\partial\alpha)-(\partial|\mathbf{G}|/\partial\alpha))}{(|\mathbf{F}|-|\mathbf{G}|)(\partial|\mathbf{G}|/\partial\alpha)}\right)^{k}$$
$$\times\sum_{\ell=0}^{M}\binom{M}{\ell}\left(\frac{-|\mathbf{G}|((\partial^2|\mathbf{F}|/\partial\beta\,\partial\alpha)-(\partial^2|\mathbf{G}|/\partial\beta\,\partial\alpha))}{(\partial|\mathbf{G}|/\partial\beta)((\partial|\mathbf{F}|/\partial\alpha)-(\partial|\mathbf{G}|/\partial\alpha))}\right)^{\ell}$$
$$\times\sum_{s=0}^{M-\ell}\binom{M-\ell}{s}\left(\frac{-|\mathbf{G}|(\partial^2|\mathbf{G}|/\partial\beta\,\partial\alpha)}{(\partial|\mathbf{G}|/\partial\beta)(\partial|\mathbf{G}|/\partial\alpha)}\right)^{s}$$
$$\times\sum_{m=0}^{P}\binom{P}{m}\left(\frac{-|\mathbf{G}|((\partial^2|\mathbf{F}|/\partial\gamma\,\partial\alpha)-(\partial^2|\mathbf{G}|/\partial\gamma\,\partial\alpha))}{(\partial|\mathbf{G}|/\partial\gamma)((\partial|\mathbf{F}|/\partial\alpha)-(\partial|\mathbf{G}|/\partial\alpha))}\right)^{m}$$
$$\times\sum_{a=0}^{P-m}\binom{P-m}{a}\Gamma[N+M+1-k-\ell-s+P-m-a]$$

$$\times \left(\frac{-|\mathbf{G}|(\partial^2|\mathbf{G}|/\partial\gamma\,\partial\beta)}{(\partial|\mathbf{G}|/\partial\gamma)(\partial|\mathbf{G}|/\partial\beta)}\right)^a$$
$$\times \sum_{b=0}^{a}\binom{a}{b}\frac{\Gamma[M-\ell-s+1]}{\Gamma[M-\ell-s-a+b+1]\Gamma[N-k-s-b+1]}$$
$$\times \left(\frac{(\partial|\mathbf{G}|/\partial\beta)}{(\partial|\mathbf{G}|/\partial\alpha)}\right)^b \sum_{t=0}^{\ell}\binom{\ell}{t}\frac{t!}{k-\ell+t}$$
$$\times \left(\frac{-((\partial|\mathbf{F}|/\partial\beta)-(\partial|\mathbf{G}|/\partial\beta))((\partial|\mathbf{F}|/\partial\alpha)-(\partial|\mathbf{G}|/\partial\alpha))}{(|\mathbf{F}|-|\mathbf{G}|)((\partial^2|\mathbf{F}|/\partial\beta\,\partial\alpha)-(\partial^2|\mathbf{G}|/\partial\beta\,\partial\alpha))}\right)^t$$
$$\times \sum_{c=0}^{m}\binom{m}{c}\frac{1}{\Gamma[k-\ell+t-m+c]}$$
$$\times \left(\frac{-((\partial|\mathbf{F}|/\partial\gamma)-(\partial|\mathbf{G}|/\partial\gamma))((\partial|\mathbf{F}|/\partial\alpha)-(\partial|\mathbf{G}|/\partial\alpha))}{(|\mathbf{F}|-|\mathbf{G}|)((\partial^2|\mathbf{F}|/\partial\gamma\,\partial\alpha)-(\partial^2|\mathbf{G}|/\partial\gamma\,\partial\alpha))}\right)^c$$
$$\times \sum_{d=0}^{c}\binom{c}{d}\frac{\Gamma[1/2+k+t+c-d]}{(t-d)!}$$
$$\times \left(\frac{\begin{pmatrix}-(|\mathbf{F}|-|\mathbf{G}|)((\partial^2|\mathbf{F}|/\partial\gamma\,\partial\beta)\\ -(\partial^2|\mathbf{G}|/\partial\gamma\,\partial\beta))\end{pmatrix}}{\begin{array}{c}\big((\partial|\mathbf{F}|/\partial\gamma)-(\partial|\mathbf{G}|/\partial\gamma)\big)\\ \times((\partial|\mathbf{F}|/\partial\beta)-(\partial|\mathbf{G}|/\partial\beta))\end{array}}\right)^d\Bigg|_{\alpha=\beta=\gamma=0}. \tag{30}$$

5.3. *Derivatives*

By differentiating determinants $|\mathbf{G}|$ and $|\mathbf{F}|$ with respect to α, β and γ and setting $\alpha=\beta=\gamma=0$ we obtain

$$\begin{aligned}\left.\frac{\partial|\mathbf{G}|}{\partial\alpha}\right|_{\substack{\alpha=0\\ \beta=0\\ \gamma=0}} &= \left.\frac{\partial|\overbrace{\mathbf{A}_{kl}+\beta\mathbf{J}_{jj}+\gamma\mathbf{J}_{ij}}^{\mathbf{C}}+\alpha\mathbf{J}_{ii}|}{\partial\alpha}\right|_{\alpha=\beta=\gamma=0}\\
&= |\mathbf{C}|\left.\frac{\partial(1+\alpha\mathrm{Tr}[\mathbf{C}^{-1}\mathbf{J}_{ii}])}{\partial\alpha}\right|_{\alpha=\beta=\gamma=0}\\
&= |\mathbf{C}|\mathrm{Tr}[\mathbf{C}^{-1}\mathbf{J}_{ii}]\big|_{\alpha=\beta=\gamma=0}\\
&= |\mathbf{A}_{kl}|\mathrm{Tr}[\mathbf{A}_{kl}^{-1}\mathbf{J}_{ii}],\end{aligned} \tag{31a}$$

$$\left.\frac{\partial|\mathbf{G}|}{\partial\beta}\right|_{\alpha=\beta=\gamma=0} = |\mathbf{A}_{kl}|\mathrm{Tr}[\mathbf{A}_{kl}^{-1}\mathbf{J}_{jj}], \tag{31b}$$

$$\left.\frac{\partial|\mathbf{G}|}{\partial\gamma}\right|_{\alpha=\beta=\gamma=0} = |\mathbf{A}_{kl}|\mathrm{Tr}[\mathbf{A}_{kl}^{-1}\mathbf{J}_{ij}], \tag{31c}$$

$$\begin{aligned}\left.\frac{\partial^2|\mathbf{G}|}{\partial\gamma\partial\alpha}\right|_{\alpha=\beta=\gamma=0} &= \left.\frac{\partial|\mathbf{C}|\mathrm{Tr}[\mathbf{C}^{-1}\mathbf{J}_{ii}]}{\partial\beta}\right|_{\alpha=\beta=\gamma=0}\\
&= \Bigg(\big|\mathbf{A}_{kl}+\gamma\mathbf{J}_{ij}\big|\mathrm{Tr}[\mathbf{A}_{kl}+\gamma\mathbf{J}_{jj}]\mathrm{Tr}[\mathbf{C}^{-1}\mathbf{J}_{ii}]\\
&\quad -|\mathbf{C}|\mathrm{Tr}\left[\mathbf{C}^{-1}\frac{\partial\mathbf{C}}{\partial\beta}\mathbf{C}^{-1}\mathbf{J}_{ii}\right]\Bigg)\Bigg|_{\alpha=\beta=\gamma=0}\\
&= |\mathbf{A}_{kl}|\big(\mathrm{Tr}[\mathbf{A}_{kl}^{-1}\mathbf{J}_{jj}]\mathrm{Tr}[\mathbf{A}_{kl}^{-1}\mathbf{J}_{ii}]\\
&\quad -\mathrm{Tr}[\mathbf{A}_{kl}^{-1}\mathbf{J}_{jj}\mathbf{A}_{kl}^{-1}\mathbf{J}_{ii}]\big),\end{aligned} \tag{32a}$$

$$\left.\frac{\partial^2|\mathbf{G}|}{\partial\gamma\partial\alpha}\right|_{\alpha=\beta=\gamma=0} = |\mathbf{A}_{kl}|\big(\mathrm{Tr}[\mathbf{A}_{kl}^{-1}\mathbf{J}_{ij}]\mathrm{Tr}[\mathbf{A}_{kl}^{-1}\mathbf{J}_{ii}] - \mathrm{Tr}[\mathbf{A}_{kl}^{-1}\mathbf{J}_{ij}\mathbf{A}_{kl}^{-1}\mathbf{J}_{ii}]\big), \tag{32b}$$

$$\left.\frac{\partial^2|\mathbf{G}|}{\partial\gamma\partial\beta}\right|_{\alpha=\beta=\gamma=0} = |\mathbf{A}_{kl}|\big(\mathrm{Tr}[\mathbf{A}_{kl}^{-1}\mathbf{J}_{ij}]\mathrm{Tr}[\mathbf{A}_{kl}^{-1}\mathbf{J}_{jj}] - \mathrm{Tr}[\mathbf{A}_{kl}^{-1}\mathbf{J}_{ij}\mathbf{A}_{kl}^{-1}\mathbf{J}_{jj}]\big). \tag{32c}$$

Expressions (31) and (32) will be satisfied if one replaces the $\mathbf{A}_{kl}$ matrix by a sum of matrices $(\mathbf{A}_{kl}+\mathbf{J}_{st})$, and the $\mathbf{G}$ matrix by the $\mathbf{F}$ matrix.

5.4. *Kinetic energy*

Before we move on to the derivation of the kinetic energy integral, let us consider some properties of the derivative operators. Let $\bar{\mathbf{B}}$ be a symmetric matrix. Then

$$\frac{\partial\mathbf{r}'\bar{\mathbf{B}}\mathbf{r}}{\partial r_\alpha} = \frac{\partial r_n\bar{B}^{nm}r_m}{\partial r_\alpha} = 2\bar{B}^{\alpha m}r_m. \tag{33}$$

From (33) one can easily obtain

$$\begin{aligned}\nabla_{\mathbf{r}}\big(\mathbf{r}'\bar{\mathbf{B}}\mathbf{r}\big) &= 2\mathbf{r}'\bar{\mathbf{B}},\\ \nabla'_{\mathbf{r}}\big(\mathbf{r}'\bar{\mathbf{B}}\mathbf{r}\big) &= 2\bar{\mathbf{B}}r.\end{aligned} \tag{34}$$

Using (34) we get

$$\begin{aligned}\nabla_{\mathbf{r}}\varphi_k &= \nabla_{\mathbf{r}}(r_i^{2n}r_j^{2m}r_{ij}^{2p}\phi_k)\\
&= \nabla_{\mathbf{r}}\Big([\mathbf{r}'(\mathbf{J}_{ii}\otimes\mathbf{I}_3)\mathbf{r}]^n[\mathbf{r}'(\mathbf{J}_{jj}\otimes\mathbf{I}_3)\mathbf{r}]^m\\
&\quad\times[\mathbf{r}'(\mathbf{J}_{ij}\otimes\mathbf{I}_3)\mathbf{r}]^p\,\mathrm{e}^{-\mathbf{r}'\bar{\mathbf{A}}_k\mathbf{r}}\Big)\\
&= \Bigg(n\frac{\nabla_{\mathbf{r}}(\mathbf{r}'\bar{\mathbf{J}}_{ii}\mathbf{r})}{r_i^2}+m\frac{\nabla_{\mathbf{r}}(\mathbf{r}'\bar{\mathbf{J}}_{jj}\mathbf{r})}{r_j^2}\\
&\quad +p\frac{\nabla_{\mathbf{r}}(\mathbf{r}'\bar{\mathbf{J}}_{ij}\mathbf{r})}{r_{ij}^2}-\nabla_{\mathbf{r}}(\mathbf{r}'\bar{\mathbf{A}}_k\mathbf{r})\Bigg)\varphi_k\\
&= 2\mathbf{r}'\left(\frac{n\bar{\mathbf{J}}_{ii}}{r_i^2}+\frac{m\bar{\mathbf{J}}_{jj}}{r_j^2}+\frac{p\bar{\mathbf{J}}_{ij}}{r_{ij}^2}-\bar{\mathbf{A}}_k\right)\varphi_k.\end{aligned} \tag{35}$$

Moreover, the derivative of the kl density function with respect to $(\bar{\mathbf{A}}_{kl})_{nm}$ gives

$$\begin{aligned}\frac{\partial}{\partial(\bar{\mathbf{A}}_{kl})_{nm}}\phi_k\phi_l &= -\phi_k\phi_l\frac{\partial\mathbf{r}'\bar{\mathbf{A}}_{kl}\mathbf{r}}{\partial(\bar{\mathbf{A}}_{kl})_{nm}}\\ &= -\phi_k\phi_l\left[r_\alpha\frac{\partial(\bar{\mathbf{A}}_{kl})^{\alpha\beta}}{\partial(\bar{\mathbf{A}}_{kl})_{nm}}r_\beta\right] \\ &= -\phi_k\phi_l r_\alpha\delta_n^\alpha\delta_m^\beta r_\beta\\ &= -\phi_k\phi_l r_n r_m.\end{aligned} \tag{36}$$

It follows from (36) that

$$\frac{\partial\phi_k\phi_l}{\partial(\mathrm{vec}\ \bar{\mathbf{A}}_{kl})'} = -\phi_k\phi_l(\mathrm{vec}\ \mathbf{rr}') \tag{37}$$

and

$$\begin{aligned}\frac{\partial\varphi_k\varphi_l}{\partial(\mathrm{vec}\ \bar{\mathbf{A}}_{kl})'} &= r_i^{2(n_k+n_l)}r_j^{2(m_k+m_l)}\\ &\quad\times r_{ij}^{2(p_k+p_l)}\frac{\partial\phi_k\phi_l}{\partial(\mathrm{vec}\ \bar{\mathbf{A}}_{kl})'} \\ &= -\varphi_k\varphi_l(\mathrm{vec}\ \mathbf{rr}'),\end{aligned} \tag{38}$$

where the vec matrix operator was defined in section 2.1. Hence,

$$\frac{\partial\varphi_k\varphi_l}{\partial(\mathrm{vec}\ \bar{\mathbf{A}}_{kl})'} = -\langle\varphi_k|(\mathrm{vec}\ \mathbf{rr}')|\varphi_l\rangle. \tag{39}$$

Finally, using (35) we can determine the kinetic energy matrix element as

$$\begin{aligned}T &= \langle\varphi_k|-\nabla_\mathbf{r}'(\mathbf{M}\otimes\mathbf{I}_3)\nabla_\mathbf{r}|\varphi_l\rangle\\ &= \left\langle\nabla_\mathbf{r}' r_i^{2n_k}r_j^{2m_k}r_{ij}^{2p_k}\phi_k\middle|\bar{\mathbf{M}}\middle|\nabla_\mathbf{r} r_i^{2n_l}r_j^{2m_l}r_{ij}^{2p_l}\phi_l\right\rangle\\ &= 4\left\langle\varphi_k\middle|\mathbf{r}'\left(\frac{n_k\bar{\mathbf{J}}_{ii}}{r_i^2}+\frac{m_k\bar{\mathbf{J}}_{jj}}{r_j^2}+\frac{p_k\bar{\mathbf{J}}_{ij}}{r_{ij}^2}-\bar{\mathbf{A}}_k\right)\right.\\ &\qquad\left.\times\bar{M}\left(\frac{n_l\bar{\mathbf{J}}_{ii}}{r_i^2}+\frac{m_l\bar{\mathbf{J}}_{jj}}{r_j^2}+\frac{p_l\bar{\mathbf{J}}_{ij}}{r_{ij}^2}-\bar{\mathbf{A}}_l\right)\mathbf{r}\varphi_l\right\rangle\\ &= 4\Big(n_kn_l\mathbf{M}_{ii}\langle\varphi_k|r_i^{-2}|\varphi_l\rangle + n_km_l\langle\varphi_k|r_i^{-2}r_j^{-2}\mathbf{r}'\bar{\mathbf{J}}_{ii}\bar{\mathbf{M}}\bar{\mathbf{J}}_{jj}\mathbf{r}|\varphi_l\rangle\\ &\qquad + n_kp_l\langle\varphi_k|r_i^{-2}r_{ij}^{-2}\mathbf{r}'\bar{\mathbf{J}}_{ii}\bar{\mathbf{M}}\bar{\mathbf{J}}_{ij}\mathbf{r}|\varphi_l\rangle\\ &\qquad + m_kn_l\langle\varphi_k|r_j^{-2}r_i^{-2}\mathbf{r}'\bar{\mathbf{J}}_{jj}\bar{\mathbf{M}}\bar{\mathbf{J}}_{ii}\mathbf{r}|\varphi_l\rangle\\ &\qquad + m_km_l\mathbf{M}_{jj}\langle\varphi_k|r_j^{-2}|\varphi_l\rangle\\ &\qquad + m_kp_l\langle\varphi_k|r_j^{-2}r_{ij}^{-2}\mathbf{r}'\bar{\mathbf{J}}_{jj}\bar{\mathbf{M}}\bar{\mathbf{J}}_{ij}\mathbf{r}|\varphi_l\rangle\\ &\qquad + p_kn_l\langle\varphi_k|r_{ij}^{-2}r_i^{-2}\mathbf{r}'\bar{\mathbf{J}}_{ij}\bar{\mathbf{M}}\bar{\mathbf{J}}_{ii}\mathbf{r}|\varphi_l\rangle\\ &\qquad + p_km_l\langle\varphi_k|r_{ij}^{-2}r_j^{-2}\mathbf{r}'\bar{\mathbf{J}}_{ij}\bar{\mathbf{M}}\bar{\mathbf{J}}_{jj}\mathbf{r}|\varphi_l\rangle\\ &\qquad + p_kp_l\langle\varphi_k|r_{ij}^{-4}\mathbf{r}'\bar{\mathbf{J}}_{ij}\bar{\mathbf{M}}\bar{\mathbf{J}}_{ij}\mathbf{r}|\varphi_l\rangle - n_k\langle\varphi_k|r_i^{-2}\mathbf{r}'\bar{\mathbf{J}}_{ii}\bar{\mathbf{M}}\bar{\mathbf{A}}_l\mathbf{r}|\varphi_l\rangle\\ &\qquad - m_k\langle\varphi_k|r_j^{-2}\mathbf{r}'\bar{\mathbf{J}}_{jj}\bar{\mathbf{M}}\bar{\mathbf{A}}_l\mathbf{r}|\varphi_l\rangle\\ &\qquad - p_k\langle\varphi_k|r_{ij}^{-2}\mathbf{r}'\bar{\mathbf{J}}_{ij}\bar{\mathbf{M}}\bar{\mathbf{A}}_l\mathbf{r}|\varphi_l\rangle - n_l\langle\varphi_k|r_i^{-2}\mathbf{r}'\bar{\mathbf{A}}_k\bar{\mathbf{M}}\bar{\mathbf{J}}_{ii}\mathbf{r}|\varphi_l\rangle\\ &\qquad - m_l\langle\varphi_k|r_j^{-2}\mathbf{r}'\bar{\mathbf{A}}_k\bar{\mathbf{M}}\bar{\mathbf{J}}_{jj}\mathbf{r}|\varphi_l\rangle\\ &\qquad - p_l\langle\varphi_k|r_{ij}^{-2}\mathbf{r}'\bar{\mathbf{A}}_k\bar{\mathbf{M}}\bar{\mathbf{J}}_{ij}\mathbf{r}|\varphi_l\rangle + \langle\varphi_k|\mathbf{r}'\bar{\mathbf{A}}_k\bar{\mathbf{M}}\bar{\mathbf{A}}_l\mathbf{r}|\varphi_l\rangle\Big).\end{aligned} \tag{40}$$

Formula (40) contains an integral involving the quadratic form $\mathbf{r}'\mathbf{Cr}$ and the terms r_i^{-2}, r_j^{-2} and r_{ij}^{-2}. Using expression (39) and including r_i^{-2}, r_j^{-2} and r_{ij}^{-2} in the *bra* or in the *ket* we can calculate all of the required integrals

$$\begin{aligned}<\varphi_k|\mathbf{r}'\mathbf{C}\mathrm{r}|\varphi_l> &= \langle\varphi_k|\mathrm{vec}\ [\mathbf{r}r']|\varphi_l\rangle\mathrm{vec}\ [\mathbf{C}]\\ &= -\frac{\partial\varphi_k\varphi_l}{\partial(\mathrm{vec}\ \bar{\mathbf{A}}_{kl})'}\ \mathrm{vec}\ [\mathbf{C}]\\ &= -\frac{\partial S}{\partial(\mathrm{vec}\ \bar{\mathbf{A}}_{kl})'}\mathrm{vec}\ [\mathbf{C}],\end{aligned} \tag{41}$$

where the derivative of the overlap integral (22) with respect to vec $\bar{\mathbf{A}}_{kl}$ is

$$\begin{aligned}\frac{\partial S}{\partial(\mathrm{vec}\ \bar{\mathbf{A}}_{kl})'} &= \frac{\partial}{\partial(\mathrm{vec}\ \bar{\mathbf{A}}_{kl})'}\\ &\times\left[\frac{2\Gamma[1/2]^{3n-1}N!M!P!}{\sqrt{|\mathbf{G}|^3}}\right.\\ &\quad\times\left(\frac{(\partial|\mathbf{G}|/\partial\alpha)}{|\mathbf{G}|}\right)^N\left(\frac{(\partial|\mathbf{G}|/\partial\beta)}{|\mathbf{G}|}\right)^M\left(\frac{(\partial|\mathbf{G}|/\partial\gamma)}{|\mathbf{G}|}\right)^P\\ &\quad\times\sum_k^M\frac{1}{k!}\left(\frac{-|\mathbf{G}|(\partial^2|\mathbf{G}|/\partial\beta\,\partial\alpha)}{(\partial|\mathbf{G}|/\partial\beta)(\partial|\mathbf{G}|/\partial\alpha)}\right)^k\\ &\quad\times\sum_{\ell=0}^P\frac{\Gamma[N+M+P+3/2-k-\ell]}{(P-\ell)!}\\ &\quad\times\left(\frac{-|\mathbf{G}|(\partial^2|\mathbf{G}|/\partial\gamma\,\partial\beta)}{(\partial|\mathbf{G}|/\partial\beta)(\partial|\mathbf{G}|/\partial\gamma)}\right)^\ell\\ &\quad\times\sum_{m=0}^\ell\frac{1}{m!(\ell-m)!(M-k-\ell+m)!(N-k-m)!}\\ &\quad\left.\times\left(\frac{(\partial|\mathbf{G}|/\partial\beta)}{(\partial|\mathbf{G}|/\partial\alpha)}\right)^m\Bigg|_{\alpha=\beta=\gamma=0}\right]\end{aligned}$$

$$= \left\{ \frac{3}{2}\frac{S}{|\mathbf{G}|}\frac{\partial|\mathbf{G}|}{\partial(\text{vec }\bar{\mathbf{A}}_{kl})'} + \frac{NS|\mathbf{G}|}{(\partial|\mathbf{G}|/\partial\alpha)}\frac{\partial[(\partial|\mathbf{G}|/\partial\alpha)/|\mathbf{G}|]}{\partial(\text{vec }\bar{\mathbf{A}}_{kl})'} \right.$$
$$+ \frac{MS|\mathbf{G}|}{(\partial|\mathbf{G}|/\partial\beta)}\frac{\partial[(\partial|\mathbf{G}|/\partial\beta)/|\mathbf{G}|]}{\partial(\text{vec }\bar{\mathbf{A}}_{kl})'}$$
$$+ \frac{PS|\mathbf{G}|}{(\partial|\mathbf{G}|/\partial\gamma)}\frac{\partial[(\partial|\mathbf{G}|/\partial\gamma)/|\mathbf{G}|]}{\partial(\text{vec }\bar{\mathbf{A}}_{kl})'}$$
$$+ \frac{2\Gamma[1/2]^{3n-1}N!M!P!}{\sqrt{|\mathbf{G}|^3}}\left(\frac{(\partial|\mathbf{G}|/\partial\alpha)}{|\mathbf{G}|}\right)^N\left(\frac{(\partial|\mathbf{G}|/\partial\beta)}{|\mathbf{G}|}\right)^M$$
$$\times\left(\frac{(\partial|\mathbf{G}|/\partial\gamma)}{|\mathbf{G}|}\right)^P\left[\sum_k^M\left(\frac{-|\mathbf{G}|(\partial^2|\mathbf{G}|/\partial\beta\,\partial\alpha)}{(\partial|\mathbf{G}|/\partial\beta)(\partial|\mathbf{G}|/\partial\alpha)}\right)^{k-1}\right.$$
$$\times\frac{1}{(k-1)!}\frac{\partial(-|\mathbf{G}|(\partial^2|\mathbf{G}|/\partial\beta\,\partial\alpha)/((\partial|\mathbf{G}|/\partial\beta)(\partial|\mathbf{G}|/\partial\alpha)))}{\partial(\text{vec }\bar{\mathbf{A}}_{kl})'}$$
$$\times\sum_{\ell=0}^P\frac{\Gamma[N+M+P+3/2-k-\ell]}{(P-\ell)!}$$
$$\times\left(\frac{-|\mathbf{G}|(\partial^2|\mathbf{G}|/\partial\gamma\,\partial\beta)}{(\partial|\mathbf{G}|/\partial\beta)(\partial|\mathbf{G}|/\partial\gamma)}\right)^\ell$$
$$\times\sum_{m=0}^\ell\frac{1}{m!(\ell-m)!(M-k-\ell+m)!(N-k-m)!}$$
$$\times\left(\frac{(\partial|\mathbf{G}|/\partial\beta)}{(\partial|\mathbf{G}|/\partial\alpha)}\right)^m + \sum_k^M\frac{1}{k!}\left(\frac{-|\mathbf{G}|(\partial^2|\mathbf{G}|/\partial\beta\,\partial\alpha)}{(\partial|\mathbf{G}|/\partial\beta)(\partial|\mathbf{G}|/\partial\alpha)}\right)^k$$
$$\times\sum_{\ell=0}^P\frac{\Gamma[N+M+P+3/2-k-\ell]\ell}{(P-\ell)!}$$
$$\times\left(\frac{-|\mathbf{G}|(\partial^2|\mathbf{G}|/\partial\gamma\,\partial\beta)}{(\partial|\mathbf{G}|/\partial\beta)(\partial|\mathbf{G}|/\partial\gamma)}\right)^{\ell-1}$$
$$\times\frac{\partial[-|\mathbf{G}|(\partial^2|\mathbf{G}|/\partial\gamma\,\partial\beta)/((\partial|\mathbf{G}|/\partial\beta)(\partial|\mathbf{G}|/\partial\gamma))]}{\partial(\text{vec }\bar{\mathbf{A}}_{kl})'}$$
$$\times\sum_{m=0}^\ell\frac{1}{m!(\ell-m)!(M-k-\ell+m)!(N-k-m)!}$$
$$\times\left(\frac{(\partial|\mathbf{G}|/\partial\beta)}{(\partial|\mathbf{G}|/\partial\alpha)}\right)^m + \sum_k^M\frac{1}{k!}\left(\frac{-|\mathbf{G}|(\partial^2|\mathbf{G}|/\partial\beta\,\partial\alpha)}{(\partial|\mathbf{G}|/\partial\beta)(\partial|\mathbf{G}|/\partial\alpha)}\right)^k$$
$$\times\sum_{\ell=0}^P\frac{\Gamma[N+M+P+3/2-k-\ell]}{(P-\ell)!}$$
$$\times\left(\frac{-|\mathbf{G}|(\partial^2|\mathbf{G}|/\partial\gamma\,\partial\beta)}{(\partial|\mathbf{G}|/\partial\beta)(\partial|\mathbf{G}|/\partial\gamma)}\right)^\ell\sum_{m=0}^\ell$$
$$\times\frac{1}{(m-1)!(\ell-m)!(M-k-\ell+m)!(N-k-m)!}$$
$$\times\left(\frac{(\partial|\mathbf{G}|/\partial\beta)}{(\partial|\mathbf{G}|/\partial\alpha)}\right)^{m-1}$$
$$\left.\left.\times\frac{\partial[(\partial|\mathbf{G}|/\partial\beta)/(\partial|\mathbf{G}|/\partial\alpha)]}{\partial(\text{vec }\bar{\mathbf{A}}_{kl})'}\right]\right\}\Bigg|_{\alpha=\beta=\gamma=0}. \quad (42)$$

Taking into account that (where we use the notation introduced in equation (8))

$$\frac{\partial}{\partial\text{vec }\mathbf{A}}\text{Tr}[\mathbf{A}^{-1}\mathbf{J}] = -\text{Tr}\left[\mathbf{A}^{-1}\frac{\partial\mathbf{A}}{\partial\text{vec }\mathbf{A}}\mathbf{A}^{-1}\mathbf{J}\right]$$
$$= -\text{vec}\left(\left[\text{Tr}\left[\left[\mathbf{A}_{ni}^{-1}\frac{\partial\mathbf{A}^{ij}}{\partial\mathbf{A}_{\alpha\beta}}\mathbf{A}_{jk}^{-1}\mathbf{J}_m^k\right]_{n\times m}\right]\right]_{\alpha\times\beta}\right)$$
$$= -\text{vec}\left(\left[\text{Tr}\left[[\mathbf{A}_{ni}^{-1}\delta_\alpha^i\delta_\beta^j\mathbf{A}_{jk}^{-1}\mathbf{J}_m^k]_{n\times m}\right]\right]_{\alpha\times\beta}\right)$$
$$= -\text{vec}\left(\left[\text{Tr}\left[[\mathbf{A}_{n\alpha}^{-1}\mathbf{A}_{\beta k}^{-1}\mathbf{J}_m^k]_{n\times m}\right]\right]_{\alpha\times\beta}\right)$$
$$= -\text{vec}\left(\left[\sum_n\mathbf{A}_{\beta k}^{-1}\mathbf{J}_n^k\mathbf{A}_{n\alpha}^{-1}\right]_{\alpha\times\beta}\right)$$
$$= -\text{vec}\left(\mathbf{A}^{-1}\mathbf{J}A^{-1}\right)', \quad (43)$$

$$\frac{\partial}{\partial\text{vec }\mathbf{A}}\text{Tr}[\mathbf{A}^{-1}\mathbf{J}\mathbf{A}^{-1}\mathbf{K}]$$
$$= -\text{Tr}\left[\mathbf{A}^{-1}\frac{\partial\mathbf{A}}{\partial\text{vec }\mathbf{A}}\mathbf{A}^{-1}\mathbf{J}\mathbf{A}^{-1}\mathbf{K}\right]$$
$$-\text{Tr}\left[\mathbf{A}^{-1}\mathbf{J}\mathbf{A}^{-1}\frac{\partial\mathbf{A}}{\partial\text{vec }\mathbf{A}}\mathbf{A}^{-1}\mathbf{K}\right]$$
$$= -\text{vec}\left[\text{Tr}\left[[\mathbf{A}_{ni}^{-1}\delta_\alpha^i\delta_\beta^j\mathbf{A}_{jk}^{-1}\mathbf{J}^{kl}\mathbf{A}_{lm}^{-1}\mathbf{K}_o^m]_{n\times o}\right]\right]_{\alpha\times\beta}$$
$$-\text{vec}\left[\text{Tr}\left[[\mathbf{A}_{ni}^{-1}\mathbf{J}^{ij}\mathbf{A}_{jk}^{-1}\delta_\alpha^k\delta_\beta^l\mathbf{A}_{lm}^{-1}\mathbf{K}_o^m]_{n\times o}\right]\right]_{\alpha\times\beta}$$
$$= -\text{vec}(\mathbf{A}^{-1}\mathbf{J}\mathbf{A}^{-1}\mathbf{K}\mathbf{A}^{-1})'$$
$$-\text{vec}(\mathbf{A}^{-1}\mathbf{K}\mathbf{A}^{-1}\mathbf{J}\mathbf{A}^{-1})', \quad (44)$$

we can find

$$\frac{\partial}{\partial(\text{vec }\bar{\mathbf{A}}_{kl})'}\frac{(\partial|\mathbf{G}|/\partial\xi)}{|\mathbf{G}|}\bigg|_{\alpha=\beta=\gamma=0} = \frac{\partial\text{Tr}[\mathbf{A}_{kl}^{-1}\mathbf{J}_\xi]}{\partial(\text{vec }\bar{\mathbf{A}}_{kl})'}$$
$$= \frac{1}{3}\frac{\partial\text{Tr}[\bar{\mathbf{A}}_{kl}^{-1}\bar{\mathbf{J}}_\xi]}{\partial(\text{vec }\bar{\mathbf{A}}_{kl})'}$$
$$= -\frac{1}{3}(\text{vec }(\bar{\mathbf{A}}_{kl}^{-1}\bar{\mathbf{J}}_\xi\bar{\mathbf{A}}_{kl}^{-1})')', \quad (45)$$

where $\xi = \{\alpha, \beta, \gamma\}$ and $\bar{\mathbf{J}}_\xi = \{\bar{\mathbf{J}}_{ii}, \bar{\mathbf{J}}_{jj}, \bar{\mathbf{J}}_{ij}\}$. Moreover, one finds that (see [7] for details)

$$\begin{aligned}\frac{\partial}{\partial(\mathrm{vec}\ \bar{\mathbf{A}}_{kl})'}|\mathbf{G}|\Big|_{\alpha=\beta=\gamma=0} &= \frac{\partial|\bar{\mathbf{A}}_{kl}|^{1/3}}{\partial(\mathrm{vec}\ \bar{\mathbf{A}}_{kl})'}\\ &= \frac{|\mathbf{A_{kl}}|^{-2/3}}{3}\frac{\partial|\mathbf{A_{kl}}|}{\partial(\mathrm{vec}\ \bar{\mathbf{A}}_{kl})'}\\ &= \frac{1}{3|\mathbf{A_{kl}}|^2}\frac{\partial|\mathbf{A_{kl}}|}{\partial\mathrm{vec}\ \bar{\mathbf{A}}_{kl}}\\ &= \frac{|\mathbf{A_{kl}}|(\mathrm{vec}\ (\bar{\mathbf{A}}_{kl}^{-1})')'}{3|\mathbf{A_{kl}}|^2}\\ &= \frac{|\mathbf{A_{kl}}|(\mathrm{vec}\ (\bar{\mathbf{A}}_{kl}^{-1})')'}{3}\end{aligned} \tag{46}$$

and

$$\begin{aligned}&\frac{\partial}{\partial(\mathrm{vec}\bar{\mathbf{A}}_{kl})'}\left(\frac{-|\mathbf{G}|(\partial^2|\mathbf{G}|/\partial\gamma\partial\beta)}{(\partial|\mathbf{G}|/\partial\beta)(\partial|\mathbf{G}|/\partial\gamma)}\right)\Big|_{\alpha=\beta=\gamma=0}\\ &=\frac{\partial(1-\{\mathrm{Tr}[\mathbf{A}_{kl}^{-1}\mathbf{J}_{ij}\mathbf{A}_{kl}^{-1}\mathbf{J}_{jj}]/(\mathrm{Tr}[\mathbf{A}_{kl}^{-1}\mathbf{J}_{ij}]\mathrm{Tr}[\mathbf{A}_{kl}^{-1}\mathbf{J}_{jj}])\})}{\partial(\mathrm{vec}\bar{\mathbf{A}}_{kl})'}\\ &=-\frac{\partial(\mathrm{Tr}[\mathbf{A}_{kl}^{-1}\mathbf{J}_{ij}\mathbf{A}_{kl}^{-1}\mathbf{J}_{jj}])\partial(\mathrm{vec}\bar{\mathbf{A}}_{kl})'}{\mathrm{Tr}[\mathbf{A}_{kl}^{-1}\mathbf{J}_{ij}]\mathrm{Tr}[\mathbf{A}_{kl}^{-1}\mathbf{J}_{jj}]}+\frac{\mathrm{Tr}[\mathbf{A}_{kl}^{-1}\mathbf{J}_{ij}\mathbf{A}_{kl}^{-1}\mathbf{J}_{jj}]}{\left(\mathrm{Tr}[\mathbf{A}_{kl}^{-1}\mathbf{J}_{ij}]\right)^2\mathrm{Tr}[\mathbf{A}_{kl}^{-1}\mathbf{J}_{jj}]}\\ &\times\frac{\partial(Tr[\mathbf{A}_{kl}^{-1}\mathbf{J}_{ij}])\partial}{\partial(\mathrm{vec}\bar{\mathbf{A}}_{kl})'}+\frac{\mathrm{Tr}[\mathbf{A}_{kl}^{-1}\mathbf{J}_{ij}\mathbf{A}_{kl}^{-1}\mathbf{J}_{jj}]}{\mathrm{Tr}[\mathbf{A}_{kl}^{-1}\mathbf{J}_{ij}]\left(\mathrm{Tr}[\mathbf{A}_{kl}^{-1}\mathbf{J}_{jj}]\right)^2}\frac{\partial\mathrm{Tr}[\mathbf{A}_{kl}^{-1}\mathbf{J}_{jj}]}{\partial\left(\mathrm{vec}\bar{\mathbf{A}}_{kl}\right)'}\\ &=\frac{(\mathrm{vec}(\bar{\mathbf{A}}_{kl}^{-1}\bar{\mathbf{J}}_{ij}\bar{\mathbf{A}}_{kl}^{-1}\bar{\mathbf{J}}_{jj}\bar{\mathbf{A}}_{kl}^{-1})')'+(\mathrm{vec}(\bar{\mathbf{A}}_{kl}^{-1}\bar{\mathbf{J}}_{jj}\bar{\mathbf{A}}_{kl}^{-1}\bar{\mathbf{J}}_{ij}\bar{\mathbf{A}}_{kl}^{-1})')'}{3\mathrm{Tr}[\mathbf{A}_{kl}^{-1}\mathbf{J}_{ij}]\mathrm{Tr}[\mathbf{A}_{kl}^{-1}\mathbf{J}_{jj}]}\\ &-\frac{\mathrm{Tr}[\mathbf{A}_{kl}^{-1}\mathbf{J}_{ij}\mathbf{A}_{kl}^{-1}\mathbf{J}_{jj}]}{3\mathrm{Tr}[\mathbf{A}_{kl}^{-1}\mathbf{J}_{ij}]\mathrm{Tr}[\mathbf{A}_{kl}^{-1}\mathbf{J}_{jj}]}\\ &\times\left(\frac{(\mathrm{vec}(\bar{\mathbf{A}}_{kl}^{-1}\bar{\mathbf{J}}_{ij}\bar{\mathbf{A}}_{kl}^{-1})')'}{\mathrm{Tr}[\mathbf{A}_{kl}^{-1}\mathbf{J}_{ij}]}+\frac{(\mathrm{vec}(\bar{\mathbf{A}}_{kl}^{-1}\bar{\mathbf{J}}_{jj}\bar{\mathbf{A}}_{kl}^{-1})')'}{\mathrm{Tr}[\mathbf{A}_{kl}^{-1}\mathbf{J}_{jj}]}\right),\end{aligned} \tag{47}$$

$$\begin{aligned}&\frac{\partial}{\partial(\mathrm{vec}\ \bar{\mathbf{A}}_{kl})'}\\ &\times\left(\frac{-|\mathbf{G}|(\partial^2|\mathbf{G}|/\partial\beta\,\partial\alpha)}{(\partial|\mathbf{G}|/\partial\beta)(\partial|\mathbf{G}|/\partial\alpha)}\right)\Big|_{\alpha=\beta=\gamma=0}=-\frac{\mathrm{Tr}[\mathbf{A}_{kl}^{-1}\mathbf{J}_{jj}\mathbf{A}_{kl}^{-1}\mathbf{J}_{ii}]}{3\mathrm{Tr}[\mathbf{A}_{kl}^{-1}\mathbf{J}_{jj}]\mathrm{Tr}[\mathbf{A}_{kl}^{-1}\mathbf{J}_{ii}]}\\ &\times\left(\frac{(\mathrm{vec}(\bar{\mathbf{A}}_{kl}^{-1}\bar{\mathbf{J}}_{jj}\bar{\mathbf{A}}_{kl}^{-1})')'}{\mathrm{Tr}[\mathbf{A}_{kl}^{-1}\mathbf{J}_{jj}]}+\frac{(\mathrm{vec}(\bar{\mathbf{A}}_{kl}^{-1}\bar{\mathbf{J}}_{ii}\bar{\mathbf{A}}_{kl}^{-1})')'}{\mathrm{Tr}[\mathbf{A}_{kl}^{-1}\mathbf{J}_{ii}]}\right)\\ &+\frac{(\mathrm{vec}(\bar{\mathbf{A}}_{kl}^{-1}\bar{\mathbf{J}}_{jj}\bar{\mathbf{A}}_{kl}^{-1}\bar{\mathbf{J}}_{ii}\bar{\mathbf{A}}_{kl}^{-1})')'+(\mathrm{vec}(\bar{\mathbf{A}}_{kl}^{-1}\bar{\mathbf{J}}_{ii}\bar{\mathbf{A}}_{kl}^{-1}\bar{\mathbf{J}}_{jj}\bar{\mathbf{A}}_{kl}^{-1})')'}{3\mathrm{Tr}[\mathbf{A}_{kl}^{-1}\mathbf{J}_{jj}]\mathrm{Tr}[\mathbf{A}_{kl}^{-1}\mathbf{J}_{ii}]},\end{aligned} \tag{48}$$

$$\begin{aligned}&\frac{\partial[(\partial|\mathbf{G}|/\partial\beta)/(\partial|\mathbf{G}|/\partial\alpha)]\big|_{\alpha=\beta=\gamma=0}}{\partial\left(\mathrm{vec}\ \bar{\mathbf{A}}_{kl}\right)'}\\ &=\frac{\partial\{|\mathbf{A_{kl}}|\mathrm{Tr}[\mathbf{A}_{kl}^{-1}\mathbf{J}_{jj}]/(|\mathbf{A_{kl}}|\mathrm{Tr}[\mathbf{A}_{kl}^{-1}\mathbf{J}_{ii}])\}}{\partial(\mathrm{vec}\ \bar{\mathbf{A}}_{kl})'}\\ &=\frac{\partial\{\mathrm{Tr}[\mathbf{A}_{kl}^{-1}\mathbf{J}_{jj}]/\mathrm{Tr}[\mathbf{A}_{kl}^{-1}\mathbf{J}_{ii}]\}}{\partial(\mathrm{vec}\ \bar{\mathbf{A}}_{kl})'}\\ &=\frac{\partial\mathrm{Tr}[\mathbf{A}_{kl}^{-1}\mathbf{J}_{jj}]}{\partial(\mathrm{vec}\ \bar{\mathbf{A}}_{kl})'}\frac{1}{\mathrm{Tr}[\mathbf{A}_{kl}^{-1}\mathbf{J}_{ii}]}\\ &-\frac{\mathrm{Tr}[\mathbf{A}_{kl}^{-1}\mathbf{J}_{jj}]}{(\mathrm{Tr}[\mathbf{A}_{kl}^{-1}\mathbf{J}_{ii}])^{-2}}\frac{\partial\mathrm{Tr}[\mathbf{A}_{kl}^{-1}\mathbf{J}_{ii}]}{\partial(\mathrm{vec}\ \bar{\mathbf{A}})'}\\ &=\frac{1}{3\mathrm{Tr}[\mathbf{A}_{kl}^{-1}\mathbf{J}_{ii}]}\\ &\quad\times\left(\frac{\mathrm{Tr}[\mathbf{A}_{kl}^{-1}\mathbf{J}_{jj}]}{\mathrm{Tr}[\mathbf{A}_{kl}^{-1}\mathbf{J}_{ii}]}(\mathrm{vec}(\bar{\mathbf{A}}_{kl}^{-1}\bar{\mathbf{J}}_{ii}\bar{\mathbf{A}}_{kl}^{-1})')'\right.\\ &\qquad\left.-(\mathrm{vec}(\bar{\mathbf{A}}_{kl}^{-1}\bar{\mathbf{J}}_{jj}\bar{\mathbf{A}}_{kl}^{-1})')'\right).\end{aligned} \tag{49}$$

It is important to note that the factor that appears before the integral (40) may make the whole term vanish if the factor becomes zero. This occurs when any power of r_α becomes zero, since the factor before the integral is proportional to the power value. For example, if $n_k + n_l = 0$ or $p_k + p_l = 0$, then $n_k p_l = 0$ and there is no need to calculate any integral that contains such a power of r_α. For example, the integral $\langle\varphi_k r_i^{-2} r_{ij}^{-2}\mathbf{r}'\bar{\mathbf{J}}_{ii}\bar{\mathbf{M}}\bar{J}_{ij}\mathbf{r}\varphi_l\rangle$ does not need to be calculated because the factor that multiplies the integral is zero.

6. Numerical implementation

In this section we discuss some aspects of the numerical implementation of the above-described integrals. The calculation of the overlap (22), potential energy (30) and kinetic energy integrals (40) and (42) involves a partial sum which can be written in the following general form:

$$f(a,x) = \sum_{k=0}^{N} a_k(-x)^k, \tag{50}$$

where $0 \le |x_k| \le 1$, a_k is a parameter function, a_0 and a_N are finite, and $\exists n, n \in [1, N-1]$, $a_{n-1} \le a_n \ge a_{n+1}$. For example, in the overlap integral, a sum of the type represented by equation (50) appears as the next to last sum in equation (22). The explicit form of the sum is $f(a,x)=\sum_{\ell=0}^{P}a_\ell(-x)^\ell$, where

$$a_\ell=\frac{\Gamma[N+M+P+3/2-k-\ell]}{(P-\ell)!}\times\sum_{m=0}^{\ell}\frac{1}{m!(\ell-m)!(M-k-\ell+m)!}\times\frac{1}{(N-k-m)!}\left(\frac{(\partial|\mathbf{G}|/\partial\beta)}{(\partial|\mathbf{G}|/\partial\alpha)}\right)^m\Bigg|_{\alpha=\beta=\gamma=0}$$

and

$$x=\frac{|\mathbf{G}|(\partial^2|\mathbf{G}|/\partial\gamma\,\partial\beta)}{(\partial|\mathbf{G}|/\partial\beta)(\partial|\mathbf{G}|/\partial\gamma)}.$$

In calculating sum (50) a problem may occur if the number of terms, N, in the summation is large and x is close to one.

In general, if a numerical algorithm is coded into a computer program and calculations are performed, the accuracy of the result is limited by the finite binary representation of the integers and real numbers in the computer system used in the calculation. Hence, the numerical result may be unstable if the computational process introduces a large numerical error. In the case of calculating the sum (50), numerical instability can be introduced by alternation of the sign of the terms corresponding to even and odd powers of $(-x)$. As a result, large numbers may need to be subtracted and the sum of the differences may be much smaller than any individual term in the sum, leading to a loss of accuracy.

The simplest approach to the numerical implementation of sum (50) can be done by performing term-by-term summation of the series. For very large values of a_k and for x close to one, such an approach usually quickly generates an overflow error even if high precision (e.g. quadruple) is used in the calculation. The relative error in the summation accumulates rapidly in each step of the procedure. Of course, one can split the summation into positive and negative subseries and subtract the two sums at the end of the calculation, but this does not usually eliminate the numerical error.

There is only one certain way to remove the accumulation of error; this is by increasing the precision of the calculations. Since, as mentioned above, non-BO molecular calculations require the use of basis functions with high powers of r_i and r_{ij}, leading to a large number of terms in the summations in the integrals, there may be a need to increase the calculation precision in the numerical implementation of the expressions derived in this work. There are various ways to increase the precision of the calculation. For example, one can use the commercial software package *The Base One Number Class*.[1] The *Base One Number Class* software includes the implementation of decimal arithmetic up to 100 significant digits in precision. Another approach could be to develop a custom-made, high-precision operator package that involves the use of an all-integer representation of the rational numbers (i.e. in the computer implementation, each number is represented as a fraction involving two integer numbers: i/k, $i,k\in I$). In an integer-based representation (i/k) the main problem which must be solved is the overflow error. Hence, in the implementation of an operation such as $+$, $-$, $*$, $/$ the high precision should be mentioned and the standard integer operators cannot be used.

The most common problem of any high-precision calculation is high memory and CPU use. This limits the types of problems which can currently be examined using such calculations. The problem described in this work may belong to this category. However, rapidly developing hardware and software computer technology may soon overcome the accuracy limitations inherent with present-day computers. The demand for computers allowing for much higher precision of calculations is growing and may soon be met by the development of new computer designs that satisfy these requirements. The algorithms presented here would certainly benefit from such a development.

7. Conclusion

In this work, we have presented algorithms for calculating the Hamiltonian and overlap matrix elements involved in non-Born–Oppenheimer calculations of molecular systems with three nuclei. The numerical implementation of the algorithms was also discussed. Since the integrals involve summations of large numbers of elements with alternating signs, their calculation may require increased computational precision. Possible options for such an increase in precision are mentioned. There are also other ways the precision problem can be circumvented. One can, for example, consider using orthogonal polynomials of powers of the distances r_1, r_2 and r_{12} as pre-exponential multipliers. Linear coefficients multiplying the r_1, r_2 and r_{12} powers in the polynomials can, perhaps, be chosen in such a way that sums of terms with alternating signs can be eliminated from the integrals. Work in this direction will be carried out in our laboratory.

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