Leading relativistic corrections for atomic P states calculated with a finite-nuclear-mass approach and all-electron explicitly correlated Gaussian functions

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Leading relativistic corrections for atomic P states calculated with a finite-nuclear-mass approach and all-electron explicitly correlated Gaussian functions.

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In this work we report progress in the development and implementation of quantum-mechanical methods for calculating bound ground and excited states of small atomic systems. The work concerns singlet states with the L=1 total orbital angular momentum (P states). The method is based on the finite-nuclear-mass (non-Born-Oppenheimer; non-BO) approach and the use of all-particle explicitly correlated Gaussian functions for expanding the non-relativistic wave function of the system. The development presented here includes derivation and implementation of algorithms for calculating the leading relativistic corrections for singlet states. The corrections are determined in the framework of the perturbation theory as expectation values of the corresponding effective operators using the non-BO wave functions. The method is tested in the calculations of the ten lowest ^1P states of the helium atom and the four lowest ^1P states of the beryllium atom.

The determination of atomic energy levels and transition frequencies with the spectroscopic precision (i.e. well below 1 cm^{-1}) as well as the corresponding wave functions remains one of the most technically and computationally challenging tasks for the quantum theory of atoms and molecules. The amount of computations required grows very rapidly with each additional electron. As a result, retaining accuracy at manageable computational cost becomes a difficult task even for few-electron systems. Many accurate methods of various nature have been developed in the electronic structure theory in the past several decades. However, in practical calculations most of them can reach only chemical accuracy (1 kcal/mol) and often cannot be applied to excited states. Yet some emerging physical problems related to precision measurements, atomic clocks, and high resolution spectroscopy require very accurate quantum-mechanical calculations that exceed chemical accuracy by several orders of magnitude.

Precise determination of the atomic energies, transition frequencies, and other basic properties requires precise calculation of the effects resulting not only from the strong Coulombic interactions between the particles, but also from more subtle effects due to relativism, quantum electrodynamics (QED), and finite nuclear mass and size. There has been a steady progress in high-precision atomic calculations over the last two decades. In 2002 very accurate calculations were reported for the lithium atom [1, 2]. In 2006-2007 works were published concerning the lowest S excitation energy of the beryllium atom [3, 4] where all-electron explicitly correlated Gaussian functions (ECGs) were used for expanding the wave functions of the system. The calculated energy of the $3^1S \rightarrow 2^1S$ transition was within the experimental error bar from the experimental value reported earlier by Johansson [5, 6]. Recently, ECGs were used to calculate the lowest $S \rightarrow P$ transitions of beryllium [7]. The calculations were performed with the infinite-nuclear-mass (INM) approach and the finite-mass effects were obtained using the perturbation theory. In that work, the leading relativistic corrections for the 2^1S, 3^1S, and 2^1P states of beryllium were calculated using the INM wave functions. We should also mentioned our recent high-accuracy calculations of the lowest four ^2S states of the boron atom [8] where similar accuracy as achieved before for four-electron atoms was reached. In those calculations the finite-nuclear-mass (FNM) approach was used. Thus, the finite-mass effect were directly incorporated in the nonrelativistic total energy, as well as in the relativistic corrections which were calculated using the first-order level of the perturbation theory with the FNM wave function being the zeroth-order solution.

In this work we report on a next step in the development of methods for precision calculations of the ground and

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excited states of small atoms. The development involves derivation and implementation of algorithms for calculating the leading relativistic corrections for atomic singlet states with the total angular momentum quantum number of one (the P states). The first-order perturbation-theory approach is used and the corrections are calculated as expectation values using the FNM wave functions expanded in terms of all-electron ECGs. The wave functions are obtained in variational calculations where the linear and non-linear parameters involved in the wave functions were extensively optimized.

We have used various types of ECG basis functions in high-accuracy atomic and molecular calculations performed with an approach where the Born-Oppenheimer (BO) approximation is not assumed [9–11]. In the calculations the coupled motion of the electrons and nuclei and the effects due to the finite masses of the nuclei (the nucleus for an atom) are described in the wave functions and the corresponding energies. When these wave functions are used in calculating the relativistic corrections, the relativistic recoil effects, etc., are directly accounted for in the results. Thus their determination does not require resorting to the perturbation theory.

ECGs are not as efficient in describing the cusps and the tail behavior of the wave functions of bound atomic and molecular states as some other types of explicitly correlated functions, such as Slaters or Hylleraas-type functions [12–16]. However, with ECGs the multi-particle integrals involved in the Hamiltonian matrix elements and in the matrix elements of the relativistic operators can be easily calculated. This allows for the use of long ECG expansions of the wave functions and effectively remediates the deficiencies of these basis functions in the atomic and molecular calculations provided the Gaussian exponential parameters are well optimized. For ECGs such optimization can be carried out very efficiently using the variational method because the expression for the total energy obtained using ECGs can be easily analytically differentiated with respect to the Gaussian exponential parameters and the energy gradient can be determined and provided to the optimization procedure [9]. The availability of the analytic gradient in the optimization helps considerably in achieving high accuracy in the calculations. It is mostly due to the implementation of the analytical energy gradient in our variational non-Born-Oppenheimer (non-BO) atomic and molecular calculations that the results concerning ground and excited states of these systems have been unmatched in accuracy by calculations performed by others. The results for the four lowest ^1P states of the beryllium atom obtained in the calculations performed in the present work provide an example of the efficiency of the gradient aided optimization approach.

I. METHOD USED IN THE CALCULATIONS

We consider an atomic system with N particles (a nucleus + $(N-1) = n$ electrons). After separating out the motion of the center of mass [10], the N-particle problem is effectively reduced to an $(N-1)$-particle problem. In the separation the total non-relativistic Hamiltonian initially expressed in terms of laboratory $3N$ Cartesian coordinates is transformed to a Hamiltonian expressed in terms of new Cartesian coordinates three of which are the laboratory coordinates of the center of mass of the system and the remaining $(3N-3)$ are internal coordinates. The origin of the internal coordinate system is placed at the nucleus. With the implementation of the new coordinates, the total Hamiltonian rigorously separates into the operator representing the kinetic energy of the motion of the center of mass and the so-called internal nonrelativistic Hamiltonian, $H_{\rm nr}$ which has the following form (in a.u.):

$$\hat{\rm H}_{\rm nr} \;=\; -\frac{1}{2}\left(\sum_{i=1}^{n}\frac{1}{\mu_i}\nabla^2_{\mathbf{r}_i}+\sum_{i=1}^{n}\sum_{j\neq i}^{n}\frac{1}{m_0}\nabla^T_{\mathbf{r}_i}\cdot\nabla_{\mathbf{r}_j}\right)+\sum_{i=1}^{n}\frac{q_0 q_i}{r_i}+\sum_{i=1}^{n}\sum_{j<i}^{n}\frac{q_i q_j}{r_{ij}}, \tag{1}$$

where q_0 is the nuclear charge, $q_i = -1, i = 1,\ldots,n$, are charges of the electrons, m_0 is the mass of the nucleus, $m_i = 1$, $i = 1,\ldots,n$ are the electron masses, and $\mu_i = m_0 m_i/(m_0+m_i)$, $i = 1,\ldots,n$ are the reduced masses of the electrons. "T" denotes the transposition. The effects of a finite nuclear mass is represented in a non-perturbative way in (1) by the mass-polarization term and the reduced masses μ_i included in the first component of the kinetic energy operator.

The most frequently used approach to account for relativistic and QED effects in light atomic systems is to expand the total energy in powers of the fine structure constant [17, 18]:

$$E_{\rm tot} = E^{(0)}_{\rm nr} + \alpha^2 E^{(2)}_{\rm rel} + \alpha^3 E^{(3)}_{\rm qed} + \ldots,$$

where $E^{(0)}_{\rm nr}$ is the nonrelativistic energy (an eigenvalue of the nonrelativistic Hamiltonian (1)), $\alpha^2 E^{(2)}_{\rm rel}$ includes the leading relativistic corrections, and $E^{(3)}_{\rm qed}$ includes the leading QED corrections. α is the fine structure parameter ($\alpha = 7.2973525698\,10^{-3}$ [19]).

$E^{(2)}_{\rm rel}$ incorporates corrections represented by the expectation values of some effective relativistic Hamiltonian, which in this wotk is the Dirac–Breit Hamiltonian in the Pauli approximation [20, 21]. The expectation values are

evaluated in the framework of the perturbation theory using the non-BO nonrelativistic wave function obtained for the considered state in the variational FNM calculation. For singlet states the relativistic Hamiltonian contains the following contributing terms,

$$\hat{H}_{\rm rel} \;=\; \hat{H}_{\rm mv} + \hat{H}_{\rm d} + \hat{H}_{\rm oo} + \hat{H}_{\rm ss}, \tag{2}$$

which represent the mass–velocity (mv), Darwin (d), orbit–orbit (oo), and spin–spin (ss) interactions (the spin-orbit interaction is zero for the siglet states). The explicit form of the $\hat{H}_{\rm mv}$, $\hat{H}_{\rm d}$, $\hat{H}_{\rm oo}$, and $\hat{H}_{\rm ss}$ Hamiltonians can be found in Ref. [10].

II. THE NOTATION

Let us first introduce the notation convention used in this work.

- α, β, ξ, etc. – lower-case Greek letters are used for scalars.
- **a**, **b**, etc. – bold font in the lower-case Latin letters is used to denote vectors in the $n \times 3$ space. These have $3n$ components. For example, $\mathbf{r}^T = (r_{1x}, r_{1y}, r_{1z}, r_{2x}, \ldots, r_{nz})$.
- A, X, etc. – upper-case Latin letters are used for matrices in the particle space. These are $n \times n$ matrices.
- $\underline{\mathbf{A}}$, $\underline{\mathbf{X}}$, etc. – bold font in upper-case Latin letters is used to denote matrices in $3n$-dimensional space. These are $3n \times 3n$ matrices.
- A^T, $\underline{\mathbf{A}}^T$ etc. – the T stands for matrix or vector transpose.
- A^{-1}, $\underline{\mathbf{A}}^{-1}$ – stands for the inverse of the matrix.
- $|A|$, $|\underline{\mathbf{A}}|$ – vertical bars stand for the determinant of the matrix. However, if the object in between the vertical bars is a vector or a scalar then the bars denote the absolute value of the vector (scalar).
- Tr A, Tr $\underline{\mathbf{A}}$ – Tr stands for the trace of the matrix.
- I_3, I_n – letter I is only used for identity matrices, so that I_3 is the 3×3 identity matrix, I_n is the $n \times n$ identity matrix, etc.

III. BASIS FUNCTIONS

The general form of the basis functions for describing the $L = 1$ states used in this work is:

$$\phi_k = z_{m_k} \exp\left[-\mathbf{r}^T \underline{\mathbf{A}}_k \mathbf{r}\right]. \tag{3}$$

Here m_k is an integer that depends on k with values from 1 to n and $\underline{\mathbf{A}}_k$ is $3n \times 3n$ symmetric matrix. $\mathbf{r}$ is a vector of the internal Cartesian coordinates of the n moving electrons (for the He and Be atoms $\mathbf{r}$ is a 6×1 and 12×1 vectors, respectively).

In the derivations we will often use the following alternative representation of the basis functions (3):

$$\phi_k = \frac{\partial}{\partial \alpha_k} \exp\left[-\mathbf{r}^T \underline{\mathbf{A}}_k \mathbf{r} + \alpha_k z_{m_k}\right]\Big|_{\alpha_k=0} = \frac{\partial}{\partial \alpha_k} \exp\left[-\mathbf{r}^T \underline{\mathbf{A}}_k \mathbf{r} + \alpha_k (\mathbf{v}^k)^T \mathbf{r}\right]\Big|_{\alpha_k=0}, \tag{4}$$

where α_k is a parameter and $\mathbf{v}^k$ is a vector whose all components are zeros, except the $3m_k$ component, which is set to 1. For example, in the case when $n = 2$ and $m_k = 1$, the six-component vector $\mathbf{v}^k$ is:

$$\mathbf{v}^k = \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ 0 \end{pmatrix} = v^k \otimes \boldsymbol{\epsilon}^z, \qquad \text{where} \qquad \boldsymbol{\epsilon}^z = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}. \tag{5}$$

Furthermore, it is convenient to define the following "generator" function that can be used to generate ϕ_k in (4) as:

$$\varphi_k = \exp\left[-\mathbf{r}^T \underline{\mathbf{A}}_k \mathbf{r} + \alpha_k (\mathbf{v}^k)^T \mathbf{r}\right]. \tag{6}$$

Basis functions used to expand wave functions of bound atomic states need to be square integrable. This puts restrictions on the $\underline{\mathbf{A}}_k$ matrix as it needs to be positive definite. To assure that $\underline{\mathbf{A}}_k$ is square definite, it is represented in our approach in the Cholesky-factored form as $\underline{\mathbf{A}}_k = (L_k L_k^T) \otimes I_3$, where L_k is a $n \times n$ lower triangular matrix, I_3 is a 3 unit matrix, and $\otimes$ denotes the Kronecker product. There are restrictions on the values of the L_k matrix elements. They can be any real numbers with values ranging from $-\infty$ to $+\infty$. Thus, the ECGs in the present approach have the form:

$$\phi_k = z_{m_k} \exp\left[-\mathbf{r}^T \left(L_k L_k^T \otimes I_3\right) \mathbf{r}\right]. \tag{7}$$

The L_k matrix elements are the non-linear exponential parameters which are variationally optimized in our calculations.

The spin-free formalism is used to implement the correct permutational symmetry and properly evaluate all necessary matrix elements. In this formalism, an appropriate symmetry projector is applied to the spatial parts of the wave function to impose the desired symmetry properties. The symmetry projector can be constructed using the standard procedure involving Young operators as described, for example, in ref. [22]. In the case of the ^1P states of the beryllium atom the permutation operator can be chosen as $(1 - P13)(1 - P24)(1 + P12)(1 + P34)$ where Pij denotes the permutation of the spatial coordinates of the i-th and j-th electrons. The above operator yields $4! = 24$ terms for the matrix elements of the Hamiltonian and overlap.

The linear coefficients, c_k, in the expansion of the wave function in terms of the basis functions and the nonlinear parameters (i.e. matrices L_k) are determined by performing a minimization of the total energy based on a multistep approach that employs the analytic energy gradient determined with respect to these parameters [10]. The variational calculations are performed separately and independently for each state, i.e. for each state a different basis set is generated.

The final basis set for each state considered in this work is generated in a multistep process. It starts with a small set of randomly chosen functions and involves incremental addition of new functions. The new functions are added to the basis set one by one and their nonlinear L_k parameters are optimized using an approach employing the analytical energy gradient. At this stage, the m_k index of z for each added function is also varied from 1 to n and the index is set equal to the value that gives the lowest energy. The initial guess for a new function is generated by selecting a subset of most contributing functions already included in the basis set, randomly perturbing their exponential parameters, and selecting, as a new function, the function from the subset which lowers the energy the most. After a certain number of functions (10-20 in the present calculations) is added to the basis set, the entire basis is reoptimized. The reoptimization involves cycling over all functions, one by one, several times and reoptimizing their nonlinear parameters. Such a one-by-one optimization process can be made very numerically efficient and it has been highly tuned in our calculations. The analytic energy gradient is also employed in this process. At each optimization step the basis set is checked for linear dependencies. If any appear, it is removed as it may cause numerical instability in the calculation.

In the test calculations performed in this work some lowest ^1P states of the He and Be atoms are considered. The calculations involving growing the basis sets for He are performed using the INM approach ($^\infty$He) and for Be using the FNM approach with the ^{7}Be nuclear mass. As our previous tests have shown, no reoptimization of the nonlinear variational parameters is needed when states of a different isotope are calculated. The adjustment of the linear coefficients, c_k, through rediagonalization of the Hamiltonian and overlap matrices is quite sufficient for describing the relatively small changes in the wave function caused by the change of the nuclear mass.

IV. PERMUTATIONAL SYMMETRY

In the calculation of the wave function expanded in terms of ECGs (3) each Gaussian is transformed with the appropriate permutational symmetry operator resulting from the total wave function (that includes and spatial and spin coordinates of the electrons) being antisymmetric with respect to the permutation of each two electron labels. The permutational symmetry operator is a sum of operators permuting the labels of the electrons multiplied by appropriate linear coefficients. Each labels-permuting operator is represented by a $3n \times 3n$ permutation matrix. Let us denote by $\underline{\mathbf{P}}$ the permutation matrix representing a particular $\hat{P}$ permutation operator. Then, acting with $\hat{P}$ on ϕ_l

we get:

$$\begin{aligned}\hat{P}\phi_l &= \hat{P}\,\frac{\partial}{\partial\alpha_l}\exp\left[-\mathbf{r}^T\underline{\mathbf{A}}_l\mathbf{r}+\alpha_l(\mathbf{v}^l)^T\mathbf{r}\right]\Big|_{\alpha_l=0}\\ &= \frac{\partial}{\partial\alpha_l}\exp\left[-\mathbf{r}^T(\underline{\mathbf{P}}^T\underline{\mathbf{A}}_l\underline{\mathbf{P}})\mathbf{r}+\alpha_l(\underline{\mathbf{P}}^T\mathbf{v}^l)^T\mathbf{r}\right]\Big|_{\alpha_l=0}.\end{aligned} \tag{8}$$

In calculating the expectation value of an operator, the following property is used:

$$\langle\hat{P}_\beta\phi_k|\hat{O}|\hat{P}_\gamma\phi_l\rangle = \langle\phi_k|\hat{O}|\hat{P}^\dagger_\beta\hat{P}_\gamma\phi_l\rangle = \langle\phi_k|\hat{O}|\hat{P}_\delta\phi_l\rangle. \tag{9}$$

The following notation is used:

$$|\tilde{\phi}_l\rangle \equiv \hat{P}|\phi_l\rangle. \tag{10}$$

The $\underline{\mathbf{A}}_l$ matrix of the non-linear parameters and the $\mathbf{v}^l$ vector for the ϕ_l basis functio are transformed in the following way (the transformed quantities are denoted as $\underline{\tilde{\mathbf{A}}}_l$ and $\tilde{\mathbf{v}}^l$): function $\tilde{\phi}_l$ are:

$$\underline{\tilde{\mathbf{A}}}_l \equiv \underline{\mathbf{P}}^T\underline{\mathbf{A}}_l\underline{\mathbf{P}}, \tag{11}$$

$$\tilde{\mathbf{v}}^l \equiv \underline{\mathbf{P}}^T\mathbf{v}^l. \tag{12}$$

V. SOME AUXILIARY FORMULAS

There are some simple relations that have been used in deriving the expressions for the integrals. They are:

1.
$$\int_{-\infty}^{+\infty}\mathrm{d}\,x\;\exp\left[-x^TAx+y^Tx\right] = \frac{\pi^{n/2}}{|A|^{1/2}}\exp\left[\frac{1}{4}y^TA^{-1}y\right]. \tag{13}$$

   The integration here is over n variables, and x is an n-component vector of these variables. y is a constant vector, $n\times n$ matrix A is assumed to be symmetric, and its real part is positive definite. Also, here and everywhere below, by the square root one should understand its principal value (i.e. that root whose real part is greater than zero).

2. The following symbols are used in the derivations:
$$\underline{\mathbf{A}}_{kl} \equiv \underline{\mathbf{A}}_k + \underline{\mathbf{A}}_l,\quad \underline{\tilde{\mathbf{A}}}_{kl} \equiv \underline{\mathbf{A}}_k + \underline{\tilde{\mathbf{A}}}_l. \tag{14}$$

3. Some useful matrix relations are used:
   - determinant derivative $\quad \mathrm{d}\,|\underline{\mathbf{X}}| = |\underline{\mathbf{X}}|\;\mathrm{Tr}\,[\underline{\mathbf{X}}^{-1}\,\mathrm{d}\,\underline{\mathbf{X}}]$, $\qquad \mathrm{d}\,|\underline{\mathbf{X}}|^{-3/2} = -\frac{3}{2}|\underline{\mathbf{X}}|^{-3/2}\;\mathrm{Tr}\,[\underline{\mathbf{X}}^{-1}\,\mathrm{d}\,\underline{\mathbf{X}}]$,
   - inverse matrix derivative $\quad \mathrm{d}\,\underline{\mathbf{X}}^{-1} = -\underline{\mathbf{X}}^{-1}(\mathrm{d}\,\underline{\mathbf{X}})\underline{\mathbf{X}}^{-1}$.

4. By $\nabla_{\mathbf{r}} = \left[\partial_x,\partial_y,\partial_z\right]$ we denote the gradient with respect to the vector of the coordinates, $\mathbf{r}$, and we have:
$$\nabla^\alpha_{\mathbf{r}}\varphi \equiv \nabla^\alpha\varphi \equiv \partial^\alpha\varphi \qquad \text{and} \qquad \nabla_{\mathbf{r}\alpha}\varphi \equiv \nabla_\alpha\varphi \equiv \partial_\alpha\varphi.$$

5. In this work we use the following first-order derivatives. For example, the derivatived of the k-function φ_k are:
$$\nabla^\alpha\varphi_k \equiv \partial^\alpha\varphi_k = \left[-2\mathbf{r}^T\underline{\mathbf{A}}_k + \alpha_k(\mathbf{v}^k)^T\right]^\alpha\varphi_k, \tag{15}$$

$$\nabla_\alpha\varphi_k \equiv \partial_\alpha\varphi_k = \left[-2\underline{\mathbf{A}}_k\mathbf{r} + \alpha_k(\mathbf{v}^k)\right]_\alpha\varphi_k. \tag{16}$$

Hence some useful relations can be derived:

$$\begin{aligned}
&\partial^\alpha\ \partial_\beta \varphi_k = \\
&= \ \left\{ -2\left(\underline{\mathbf{A}}_k\right)_\beta^{\ \alpha} + 4\ \left(\mathbf{r}^T\underline{\mathbf{A}}_k\right)^\alpha \left(\underline{\mathbf{A}}_k\mathbf{r}\right)_\beta - 2\alpha_k\ \left(\mathbf{r}^T\underline{\mathbf{A}}_k\right)^\alpha (\mathbf{v}^k)_\beta - 2\alpha_k(\mathbf{v}^k)^\alpha \left(\underline{\mathbf{A}}_k\mathbf{r}\right)_\beta + \alpha_k^2(\mathbf{v}^k)^\alpha(\mathbf{v}^k)_\beta \right\}\varphi_k, \qquad (17)\\
&\partial_\alpha\ \partial_\beta \varphi_k = \\
&= \ \left\{ -2\left(\underline{\mathbf{A}}_k\right)_{\alpha\,\beta} + 4\ \left(\underline{\mathbf{A}}_k\mathbf{r}\right)_\alpha \left(\underline{\mathbf{A}}_k\mathbf{r}\right)_\beta - 2\alpha_k\ \left(\underline{\mathbf{A}}_k\mathbf{r}\right)_\alpha (\mathbf{v}^k)_\beta - 2\alpha_k(\mathbf{v}^k)_\alpha \left(\underline{\mathbf{A}}_k\mathbf{r}\right)_\beta + \alpha_k^2(\mathbf{v}^k)_\alpha(\mathbf{v}^k)_\beta \right\}\varphi_k, \qquad (18)
\end{aligned}$$

$$\begin{aligned}
\left(\underline{\mathbf{D}}\nabla\right)_\beta \varphi_k \ &= \ \underline{\mathbf{D}}_\beta^{\ \alpha}\partial_\alpha\varphi_k = \left[-2\underline{\mathbf{D}}\ \underline{\mathbf{A}}_k\mathbf{r} + \alpha_k\underline{\mathbf{D}}(\mathbf{v}^k)\right]_\beta \varphi_k, \qquad (19)\\
\left(\nabla^T\underline{\mathbf{D}}\right)^\beta \varphi_k \ &= \ \underline{\mathbf{D}}_\alpha^{\ \beta}\partial^\alpha\varphi_k = \left[-2\mathbf{r}^T\underline{\mathbf{A}}_k\ \underline{\mathbf{D}} + \alpha_k(\mathbf{v}^k)^T\underline{\mathbf{D}}\right]^\beta \varphi_k, \qquad (20)\\
\nabla^T\underline{\mathbf{D}}\nabla\varphi_k \ &= \ \left\{ -2\ \mathrm{Tr}\ \left[\underline{\mathbf{A}}_k\underline{\mathbf{D}}\right] + 4\ \left(\mathbf{r}^T\underline{\mathbf{A}}_k\ \underline{\mathbf{D}}\ \underline{\mathbf{A}}_k\mathbf{r}\right) - 2\alpha_k\ \left(\mathbf{r}^T\underline{\mathbf{A}}_k\ \underline{\mathbf{D}}\ \mathbf{v}^k\right) - 2\alpha_k\left(\mathbf{v}^k\ \underline{\mathbf{D}}\ \underline{\mathbf{A}}_k\mathbf{r}\right) + \alpha_k^2\left(\mathbf{v}^k\ \underline{\mathbf{D}}\ \mathbf{v}^k\right)\right\}\varphi_k. \qquad (21)
\end{aligned}$$

$$\begin{aligned}
&\partial^\rho\partial_\beta\ \partial_\alpha\varphi_k = \\
&= \Big[+4\ \left(\underline{\mathbf{A}}_k\right)_\alpha^\rho \left(\underline{\mathbf{A}}_k\mathbf{r}\right)_\beta + 4\ \left(\underline{\mathbf{A}}_k\right)_\beta^\rho \left(\underline{\mathbf{A}}_k\mathbf{r}\right)_\alpha - 2\alpha_k\ \left(\underline{\mathbf{A}}_k\right)_\alpha^\rho (\mathbf{v}^k)_\beta - 2\alpha_k\left(\underline{\mathbf{A}}_k\right)_\beta^\rho (\mathbf{v}^k)_\alpha + 4\left(\underline{\mathbf{A}}_k\right)_{\alpha\,\beta}\left(\mathbf{r}^T\underline{\mathbf{A}}_k\right)^\rho \ + \\
&\quad -8\left(\underline{\mathbf{A}}_k\mathbf{r}\right)_\alpha \left(\underline{\mathbf{A}}_k\mathbf{r}\right)_\beta \left(\mathbf{r}^T\underline{\mathbf{A}}_k\right)^\rho + 4\alpha_k\ \left(\underline{\mathbf{A}}_k\mathbf{r}\right)_\alpha (\mathbf{v}^k)_\beta \left(\mathbf{r}^T\underline{\mathbf{A}}_k\right)^\rho + 4\alpha_k(\mathbf{v}^k)_\alpha \left(\underline{\mathbf{A}}_k\mathbf{r}\right)_\beta \left(\mathbf{r}^T\underline{\mathbf{A}}_k\right)^\rho - 2\alpha_k^2(\mathbf{v}^k)_\alpha(\mathbf{v}^k)_\beta \left(\mathbf{r}^T\underline{\mathbf{A}}_k\right)^\rho \\
&\quad -2\alpha_k\ \left(\mathbf{v}^{kT}\right)^\rho \left(\underline{\mathbf{A}}_k\right)_{\alpha\,\beta} + 4\alpha_k\ \left(\mathbf{v}^{kT}\right)^\rho \left(\underline{\mathbf{A}}_k\mathbf{r}\right)_\alpha \left(\underline{\mathbf{A}}_k\mathbf{r}\right)_\beta - 2\alpha_k^2\ \left(\mathbf{v}^{kT}\right)^\rho \left(\underline{\mathbf{A}}_k\mathbf{r}\right)_\alpha (\mathbf{v}^k)_\beta + \\
&\quad -2\alpha_k^2\left(\mathbf{v}^{kT}\right)^\rho (\mathbf{v}^k)_\alpha \left(\underline{\mathbf{A}}_k\mathbf{r}\right)_\beta + \alpha_k^3\left(\mathbf{v}^{kT}\right)^\rho (\mathbf{v}^k)_\alpha(\mathbf{v}^k)_\beta \Big]\varphi_k. \qquad (22)
\end{aligned}$$

6. The matrix $\underline{\mathbf{J}}_{ij}$ used in the above expressions is defined as:

$$\underline{\mathbf{J}}_{ij} = \left\{ \begin{array}{cc} \underline{\mathbf{E}}_{ii} & i = j \\ \underline{\mathbf{E}}_{ii} + \underline{\mathbf{E}}_{jj} - \underline{\mathbf{E}}_{ij} - \underline{\mathbf{E}}_{ji} & i \neq j \end{array} \right\},$$

where $\underline{\mathbf{E}}_{ij}$ is the $3n \times 3n$ matrix with 1 in the ij-th position and 0's elsewhere. Formally this can be written as: $(E_{ij})^\alpha_{\ \beta} = \delta_i^{\ \alpha}\ \delta_{j\,\beta}$.

7. Transformations involving determinants can be be handled using the following theorem [23]:

$$\begin{aligned}
|I_n + \alpha\ H_1| \ &= \ 1 + \alpha \mathrm{Tr}[H_1] \qquad (23)\\
|I_n + \alpha\ H_1 + \beta\ H_2| \ &= \ 1 + \alpha\mathrm{Tr}[H_1] + \beta\mathrm{Tr}[H_2] + \alpha\beta\left(\mathrm{Tr}[H_1]\mathrm{Tr}[H_2] - \mathrm{Tr}[H_1 f H_2]\right). \qquad (24)
\end{aligned}$$

8. Inverse of a sum of Matrices

- If A is an arbitrary non-singular square matrix and B is a non-singular matrix with rank one then: [23]

$$(A+B)^{-1} = A^{-1} - \frac{A^{-1}BA^{-1}}{1 + \mathrm{Tr}\left[BA^{-1}\right]}. \qquad (25)$$

- Sum of two Kronecker products, $A \otimes G + B \otimes E$, where B, E are matrices of rank one and A and G are nonsingular matrices:

$$(A \otimes G + B \otimes E)^{-1} = A^{-1} \otimes G^{-1} - \frac{1}{1 + \mathrm{Tr}[EG^{-1}]\ \mathrm{Tr}[BA^{-1}]}\ A^{-1}BA^{-1} \otimes G^{-1}E\ G^{-1}. \qquad (26)$$

VI. HAMILTONIAN

The relativistic Hamiltonian for singlet states used in this work (see Eq. 2) consists of the following terms:

$$\hat{\mathrm{H}}_{\mathrm{mv}} = -\frac{1}{8}\left[\frac{1}{m_0^3}\left(\sum_{i=1}^{n}\nabla_{\mathbf{r}_i}\right)^4 + \sum_{i=1}^{n}\frac{1}{m_i^3}\,\nabla_{\mathbf{r}_i}^4\right], \tag{27}$$

$$\hat{\mathrm{H}}_{\mathrm{dar}} = \frac{\pi}{2}\sum_{i=1}^{n}\left(\frac{1}{m_0^2}+\frac{1}{m_i^2}\right) q_0 q_i\;\delta^3(\mathbf{r}_i) \;+\frac{\pi}{2}\sum_{i=1}^{n}\sum_{j\neq i}^{n}\frac{1}{m_i^2}\,q_i q_j\;\delta^3(\mathbf{r}_{ij})\,, \tag{28}$$

$$\begin{aligned}\hat{\mathrm{H}}_{\mathrm{oo}} = &-\frac{1}{2}\sum_{i=i}^{n}\frac{q_0 q_i}{m_0 m_i}\left\{\frac{1}{r_i}\nabla_{\mathbf{r}_i}^T\cdot\nabla_{\mathbf{r}_i}+\frac{1}{r_i^3}\mathbf{r}_i^T\cdot(\mathbf{r}_i^T\cdot\nabla_{\mathbf{r}_i})\nabla_{\mathbf{r}_i}\right\}+\\ &-\frac{1}{2}\sum_{i=1}^{n}\sum_{j\neq i}^{n}\frac{q_0 q_i}{m_0 m_i}\left\{\frac{1}{r_i}\nabla_{\mathbf{r}_i}^T\cdot\nabla_{\mathbf{r}_j}+\frac{1}{r_i^3}\mathbf{r}_i^T\cdot(\mathbf{r}_i^T\cdot\nabla_{\mathbf{r}_j})\nabla_{\mathbf{r}_i}\right\}+\\ &+\frac{1}{2}\sum_{i=1}^{n}\sum_{j>i}^{n}\frac{q_i q_j}{m_i m_j}\left\{\frac{1}{r_{ij}}\nabla_{\mathbf{r}_i}^T\cdot\nabla_{\mathbf{r}_j}+\frac{1}{r_{ij}^3}\mathbf{r}_{ij}^T\cdot(\mathbf{r}_{ij}^T\cdot\nabla_{\mathbf{r}_i})\nabla_{\mathbf{r}_j}\right\}.\end{aligned} \tag{29}$$

All these terms are treated as perturbations.

VII. MASS-VELOCITY HAMILTONIAN MATRIX ELEMENT

$$\langle\phi_k|\,\hat{\mathrm{H}}_{\mathrm{mv}}\,|\tilde{\phi}_l\rangle = -\frac{1}{8}\left[\frac{1}{m_0^3}\,\langle\phi_k|\left(\sum_{i=1}^{n}\nabla_{\mathbf{r}_i}\right)^4|\tilde{\phi}_l\rangle + \sum_{i=1}^{n}\frac{1}{m_i^3}\,\langle\phi_k|\,\nabla_{\mathbf{r}_i}^4\,|\tilde{\phi}_l\rangle\right], \tag{30}$$

The matrix elements that need to be calculated are:

$$\langle\phi_k|\hat{\mathrm{H}}_{\mathrm{mv}}|\tilde{\phi}_l\rangle = -\frac{1}{8}\left(\frac{1}{m_0^3}\langle\nabla_{\mathbf{r}}^T\underline{\mathbf{J}}\nabla_{\mathbf{r}}\phi_k\mid\nabla_{\mathbf{r}}^T\underline{\mathbf{J}}\nabla_{\mathbf{r}}\tilde{\phi}_l\rangle+\sum_{i=1}^{n}\frac{1}{m_i^3}\langle\nabla_{\mathbf{r}}^T\underline{\mathbf{J}}_{ii}\nabla_{\mathbf{r}}\phi_k\mid\nabla_{\mathbf{r}}^T\underline{\mathbf{J}}_{ii}\nabla_{\mathbf{r}}\tilde{\phi}_l\rangle\right), \tag{31}$$

where we use matrix $\underline{\mathbf{J}}$ (with no indicies), whose all matrix elements are equal to ones: $\underline{\mathbf{J}}_{\alpha\beta}=1$.

Only one type of integral appears in the expression for the $\hat{\mathrm{H}}_{\mathrm{mv}}$ matrix elements: $\langle\nabla_{\mathbf{r}}{}^T\underline{\mathbf{D}}\nabla_{\mathbf{r}}\phi_k|\nabla_{\mathbf{r}}{}^T\underline{\mathbf{D}}\nabla_{\mathbf{r}}\tilde{\phi}_l\rangle$, where $\underline{\mathbf{D}}$ is either $\underline{\mathbf{J}}$ or $\underline{\mathbf{J}}_{ii}$. To compute it we express it, according with (21), through the following elementary integrals:

$$\begin{aligned}&\langle\nabla_{\mathbf{r}}{}^T\underline{\mathbf{D}}\nabla_{\mathbf{r}}\phi_k\mid\nabla_{\mathbf{r}}{}^T\underline{\mathbf{D}}\nabla_{\mathbf{r}}\tilde{\phi}_l\rangle = \frac{\partial}{\partial\alpha_k}\frac{\partial}{\partial\alpha_l}\langle\nabla_{\mathbf{r}}{}^T\underline{\mathbf{D}}\nabla_{\mathbf{r}}\varphi_k\mid\nabla_{\mathbf{r}}{}^T\underline{\mathbf{D}}\nabla_{\mathbf{r}}\tilde{\varphi}_l\rangle\Big|_{\alpha_k=\alpha_l=0} =\\ =\;&36\;\mathrm{Tr}\,[A_kD]\;\mathrm{Tr}\,[\tilde{A}_lD]\;\langle\phi_k|\tilde{\phi}_l\rangle - 24\;\mathrm{Tr}\,[\tilde{A}_lD]\langle\phi_k|\mathbf{r}^T\underline{\mathbf{A}}_k\underline{\mathbf{D}}\;\underline{\mathbf{A}}_k\mathbf{r}|\tilde{\phi}_l\rangle + 16\langle\phi_k|\left(\mathbf{r}^T\underline{\mathbf{A}}_k\underline{\mathbf{D}}\;\underline{\mathbf{A}}_k\mathbf{r}\right)\;\left(\mathbf{r}^T\underline{\tilde{\mathbf{A}}}_l\underline{\mathbf{D}}\;\underline{\tilde{\mathbf{A}}}_l\mathbf{r}\right)|\tilde{\phi}_l\rangle +\\ &+12\;\;\mathrm{Tr}\,[A_kD]\langle\varphi_k|\left(\mathbf{v}^{kT}\mathbf{r}\right)\left(\mathbf{r}^T\underline{\mathbf{A}}_l\underline{\mathbf{D}}\tilde{\mathbf{v}}^l\right)|\tilde{\varphi}_l\rangle + 12\;\mathrm{Tr}\,[A_kD]\langle\varphi_k|\left(\mathbf{v}^{kT}\mathbf{r}\right)\left(\mathbf{r}^T\underline{\mathbf{A}}_l\underline{\mathbf{D}}\tilde{\mathbf{v}}^l\right)|\tilde{\varphi}_l\rangle + 12\;\;\mathrm{Tr}\,[A_lD]\langle\varphi_k|\left(\mathbf{r}^T\underline{\mathbf{A}}_k\underline{\mathbf{D}}\mathbf{v}^k\right)\left(\tilde{\mathbf{v}}^{lT}\mathbf{r}\right)|\tilde{\varphi}_l\rangle\\ &+12\;\;\mathrm{Tr}\,[A_lD]\;\langle\varphi_k|\left(\mathbf{v}^{kT}\underline{\mathbf{D}\mathbf{A}}_k\mathbf{r}\right)\left(\tilde{\mathbf{v}}^{lT}\mathbf{r}\right)|\tilde{\varphi}_l\rangle.\end{aligned} \tag{32}$$

VIII. DARWIN HAMILTONIAN MATRIX ELEMENT

$$\langle\phi_k|\,\hat{H}_{\mathrm{dar}}\,|\tilde{\phi}_l\rangle = \frac{\pi}{2}\sum_{i=1}^{n}\left(\frac{1}{m_0^2}+\frac{1}{m_i^2}\right) q_0 q_i\;\langle\phi_k\mid\delta^3(\mathbf{r}_i)\mid\tilde{\phi}_l\rangle \;+\frac{\pi}{2}\sum_{i=1}^{n}\sum_{j\neq i}^{n}\frac{1}{m_i^2}\,q_i q_j\;\langle\phi_k\mid\delta^3(\mathbf{r}_{ij})\mid\tilde{\phi}_l\rangle\,. \tag{33}$$

The contributing integrals to this matrix elements are calculated as:

$$\langle \phi_k \mid \delta^3(\mathbf{r}_g) \mid \tilde{\phi}_l \rangle \;=\; \frac{\mathsf{S}_{kl}}{\pi^{3/2}\,\mathrm{Tr}\,[\tilde{A}_{kl}^{-1} J_g]^{3/2}} \left\{ 1 - \frac{1}{\mathrm{Tr}\,[\tilde{A}_{kl}^{-1} J_g]} \frac{v^{k\prime} \tilde{A}_{kl}^{-1} J_g \tilde{A}_{kl}^{-1} \tilde{v}^l}{v^{k\prime} \tilde{A}_{kl}^{-1} \tilde{v}^l} \right\}, \tag{34}$$

where $J_g = J_{ii}$ or $J_g = J_{ij}$. Matrix elements with the Dirac delta function were calculated in our previous work [24]

IX. ORBIT-ORBIT HAMILTONIAN MATRIX ELEMENT

The matrix notation of the orbit-orbit interaction operator is (for details see [25, 26]):

$$\langle \phi_k \mid \hat{\mathrm{H}}_{\mathrm{oo}} \mid \tilde{\phi}_l \rangle =$$

$$-\frac{1}{2} \sum_{i=1}^{n} \frac{q_0 q_i}{m_0 m_i} \;\langle \phi_k \mid \frac{1}{r_i} \nabla^T \underline{\mathbf{E}}_{ii} \nabla - \left(\mathbf{r}^T \underline{\mathbf{E}}_{ii} \right)^{\alpha} \left(\nabla^T \underline{\mathbf{E}}_{ii} \frac{1}{r_i} \right)^{\beta} \left(\underline{\mathbf{E}}_{ii} \nabla \right)_{\beta} \left(\underline{\mathbf{E}}_{ii} \nabla \right)_{\alpha} \mid \tilde{\phi}_l \rangle + \tag{35}$$

$$-\frac{1}{2} \sum_{i=1}^{n} \sum_{j \neq i}^{n} \frac{q_0 q_i}{m_0 m_i} \;\langle \phi_k \mid \frac{1}{r_i} \nabla^T \underline{\mathbf{E}}_{ij} \nabla - \left(\mathbf{r}^T \underline{\mathbf{E}}_{ii} \right)^{\alpha} \left(\nabla^T \underline{\mathbf{E}}_{ij} \frac{1}{r_i} \right)^{\beta} \left(\underline{\mathbf{E}}_{jj} \nabla \right)_{\beta} \left(\underline{\mathbf{E}}_{ii} \nabla \right)_{\alpha} \mid \tilde{\phi}_l \rangle + \tag{36}$$

$$+\frac{1}{2} \sum_{i=1}^{n} \sum_{j>i}^{n} \frac{q_i q_j}{m_i m_j} \;\langle \phi_k \mid \frac{1}{r_{ij}} \nabla^T \underline{\mathbf{E}}_{ij} \nabla + \left(\mathbf{r}^T (\underline{\mathbf{E}}_{ij} - \underline{\mathbf{E}}_{jj}) \right)^{\alpha} \left(\nabla^T \underline{\mathbf{E}}_{ji} \frac{1}{r_{ij}} \right)^{\beta} \left(\underline{\mathbf{E}}_{ii} \nabla \right)_{\beta} \left(\underline{\mathbf{E}}_{jj} \nabla \right)_{\alpha} \mid \tilde{\phi}_l \rangle. \tag{37}$$

To simplify the expression for the expectation value of $\hat{\mathrm{H}}_{\mathrm{oo}}$ we use the following general integral for each of the three terms appearing in the expectation value:

$$\langle \phi_k | \, \frac{1}{r_g} \nabla^T \, \underline{\mathbf{B}} \, \nabla | \, \tilde{\phi}_l \rangle - \langle \phi_k | \, \left(\mathbf{r}^T \, \underline{\mathbf{K}} \right)^{\alpha} \left(\nabla^T \underline{\mathbf{D}} \, \frac{1}{r_g} \right)^{\beta} \left(\, \underline{\mathbf{F}} \, \nabla \right)_{\beta} \left(\, \underline{\mathbf{G}} \, \nabla \right)_{\alpha} | \tilde{\phi}_l \rangle = \tag{38}$$

$$= \; \frac{\partial}{\partial \alpha_k} \frac{\partial}{\partial \alpha_l} \langle \varphi_k | \, \frac{1}{r_g} \nabla^T \, \underline{\mathbf{B}} \, \nabla | \, \tilde{\varphi}_l \rangle \Big|_{\alpha_k = \alpha_l = 0} - \frac{\partial}{\partial \alpha_k} \frac{\partial}{\partial \alpha_l} \langle \varphi_k | \, \left(\mathbf{r}^T \, \underline{\mathbf{K}} \right)^{\alpha} \left(\nabla^T \underline{\mathbf{D}} \, \frac{1}{r_g} \right)^{\beta} \left(\, \underline{\mathbf{F}} \, \nabla \right)_{\beta} \left(\, \underline{\mathbf{G}} \, \nabla \right)_{\alpha} | \tilde{\varphi}_l \rangle \Big|_{\alpha_k = \alpha_l = 0} \tag{39}$$

where

$$\begin{array}{lllllll} \text{for the term (35):} & g = i & \underline{\mathbf{B}} = \underline{\mathbf{E}}_{ii} & \underline{\mathbf{K}} = \underline{\mathbf{E}}_{ii} & \underline{\mathbf{D}} = \underline{\mathbf{E}}_{ii} & \underline{\mathbf{F}} = \underline{\mathbf{E}}_{ii} & \underline{\mathbf{G}} = \underline{\mathbf{E}}_{ii}, \\ \text{for term (36):} & g = i & \underline{\mathbf{B}} = \underline{\mathbf{E}}_{ij} & \underline{\mathbf{K}} = \underline{\mathbf{E}}_{ii} & \underline{\mathbf{D}} = \underline{\mathbf{E}}_{ij} & \underline{\mathbf{F}} = \underline{\mathbf{E}}_{jj} & \underline{\mathbf{G}} = \underline{\mathbf{E}}_{ii}, \\ \text{for the term (37):} & g = ij & \underline{\mathbf{B}} = \underline{\mathbf{E}}_{ij} & \underline{\mathbf{K}} = (\, \underline{\mathbf{E}}_{ij} - \underline{\mathbf{E}}_{jj}) & \underline{\mathbf{D}} = \underline{\mathbf{E}}_{ji} & \underline{\mathbf{F}} = \underline{\mathbf{E}}_{ii} & \underline{\mathbf{G}} = \underline{\mathbf{E}}_{jj}. \end{array} \tag{40}$$

Now, the integrals appearing in the above matrix elements are expressed in terms more elemental integrals. After that these elemental integrals are calculated.

A. Integral $\langle \phi_k | \, \frac{1}{r_g} \nabla^T \, \underline{\mathbf{B}} \, \nabla | \, \tilde{\phi}_l \rangle$

$$\langle \phi_k | \, \frac{1}{r_g} \nabla^T \, \underline{\mathbf{B}} \, \nabla | \, \tilde{\phi}_l \rangle \;=\; \frac{\partial}{\partial \alpha_k} \frac{\partial}{\partial \alpha_l} \langle \varphi_k | \, \frac{1}{r_g} \nabla^T \, \underline{\mathbf{B}} \, \nabla | \, \tilde{\varphi}_l \rangle \Big|_{\alpha_k = \alpha_l = 0}. \tag{41}$$

Based on (21) we have:

$$\nabla^T \, \underline{\mathbf{B}} \, \nabla \tilde{\varphi}_l = \partial^{\alpha} \, \underline{\mathbf{B}}_{\alpha}{}^{\beta} \partial_{\beta} \tilde{\varphi}_l =$$

$$= \; \left\{ -2 \, \mathrm{Tr} \, [\, \underline{\tilde{\mathbf{A}}}_l \, \underline{\mathbf{B}} \,] + 4 \, \left(\mathbf{r}^T \underline{\tilde{\mathbf{A}}}_l \, \underline{\mathbf{B}} \, \underline{\tilde{\mathbf{A}}}_l \mathbf{r} \right) - 2\alpha_l \, \left(\mathbf{r}^T \underline{\tilde{\mathbf{A}}}_l \, \underline{\mathbf{B}} \, \tilde{\mathbf{v}}^l \right) - 2\alpha_l \left(\mathbf{v}^{lT} \, \underline{\mathbf{B}} \, \underline{\tilde{\mathbf{A}}}_l \mathbf{r} \right) + \alpha_l^2 \left(\tilde{\mathbf{v}}^{lT} \, \underline{\mathbf{B}} \, \tilde{\mathbf{v}}^l \right) \right\} \tilde{\varphi}_l \tag{42}$$

and

$$\frac{\partial}{\partial \alpha_k} \frac{\partial}{\partial \alpha_l} \langle \varphi_k | \, \frac{1}{r_g} \nabla^T \, \underline{\mathbf{B}} \, \nabla | \, \tilde{\varphi}_l \rangle \Big|_{\alpha_k = \alpha_l = 0} \;=\; -6 \, \mathrm{Tr} \, [\, \tilde{A}_l B \,] \, \langle \phi_k | \, \frac{1}{r_g} \, | \tilde{\phi}_l \rangle + 4 \, \langle \phi_k | \, \frac{1}{r_g} \, \left(\mathbf{r}^T \underline{\mathbf{A}}_l \, \underline{\mathbf{B}} \, \underline{\tilde{\mathbf{A}}}_l \mathbf{r} \right) \, | \tilde{\phi}_l \rangle +$$

$$-2 \, \langle \varphi_k | \, \frac{1}{r_g} \, \left(\mathbf{v}^{kT} \mathbf{r} \right) \, \left(\mathbf{r}^T \underline{\tilde{\mathbf{A}}}_l \, \underline{\mathbf{B}} \, \tilde{\mathbf{v}}^l \right) \, | \tilde{\varphi}_l \rangle - 2 \, \langle \varphi_k | \, \frac{1}{r_g} \, \left(\mathbf{v}^{kT} \mathbf{r} \right) \, \left(\tilde{\mathbf{v}}^{lT} \, \underline{\mathbf{B}} \, \underline{\tilde{\mathbf{A}}}_l \mathbf{r} \right) \, | \tilde{\varphi}_l \rangle. \tag{43}$$

B. Integral $\langle\phi_k|\ \left(\mathbf{r}^T\ \underline{\mathbf{K}}\right)^\alpha \left(\nabla^T \underline{\mathbf{D}}\ \frac{1}{r_g}\right)^\beta \left(\ \underline{\mathbf{F}}\ \nabla\right)_\beta \left(\ \underline{\mathbf{G}}\ \nabla\right)_\alpha |\tilde{\phi}_l\rangle$

$$\langle\phi_k|\ \left(\mathbf{r}^T\ \underline{\mathbf{K}}\right)^\alpha \left(\nabla^T \underline{\mathbf{D}}\ \frac{1}{r_g}\right)^\beta \left(\ \underline{\mathbf{F}}\ \nabla\right)_\beta \left(\ \underline{\mathbf{G}}\ \nabla\right)_\alpha |\tilde{\phi}_l\rangle = \frac{\partial}{\partial\alpha_k}\frac{\partial}{\partial\alpha_l}\langle\varphi_k|\ \left(\mathbf{r}^T\ \underline{\mathbf{K}}\right)^\alpha \left(\nabla^T \underline{\mathbf{D}}\ \frac{1}{r_g}\right)^\beta \left(\ \underline{\mathbf{F}}\ \nabla\right)_\beta \left(\ \underline{\mathbf{G}}\ \nabla\right)_\alpha |\tilde{\varphi}_l\rangle\Big|_{\alpha_k=\alpha_l=0}.$$

We rewrite this integral in the following way:

$$\langle\varphi_k|\ \left(\mathbf{r}^T\ \underline{\mathbf{K}}\right)^\alpha \left(\nabla^T\ \underline{\mathbf{D}}\ \frac{1}{r_g}\right)^\beta \left(\ \underline{\mathbf{F}}\ \nabla\right)_\beta \left(\ \underline{\mathbf{G}}\ \nabla\right)_\alpha |\tilde{\varphi}_l\rangle = -\int \mathrm{d}\mathbf{r}\ \frac{1}{r_g}\ \left(\nabla^T\ \underline{\mathbf{D}}\right)^\beta \left\{\varphi_k\ \left(\mathbf{r}^T\ \underline{\mathbf{K}}\right)^\alpha \left(\ \underline{\mathbf{F}}\ \nabla\right)_\beta \left(\ \underline{\mathbf{G}}\ \nabla\right)_\alpha \tilde{\varphi}_l\right\},$$

the integral can be split into three terms:

$$\begin{aligned}
&-\int \mathrm{d}\mathbf{r}\ \frac{1}{r_g}\ \left(\nabla^T\ \underline{\mathbf{D}}\right)^\beta \left\{\varphi_k\ \left(\mathbf{r}^T\ \underline{\mathbf{K}}\right)^\alpha\ \left(\ \underline{\mathbf{F}}\ \nabla\right)_\beta \left(\ \underline{\mathbf{G}}\ \nabla\right)_\alpha \tilde{\varphi}_l\right\} = \\
= &-\int \mathrm{d}\mathbf{r}\ \frac{1}{r_g}\ \left\{\left(\nabla^T\ \underline{\mathbf{D}}\right)^\beta \varphi_k\right\}\ \left(\mathbf{r}^T\ \underline{\mathbf{K}}\ \underline{\mathbf{G}}\ \nabla\right)\left(\ \underline{\mathbf{F}}\ \nabla\right)_\beta \tilde{\varphi}_l \qquad \equiv \quad \text{- term1} \\
&-\int \mathrm{d}\mathbf{r}\ \frac{1}{r_g}\ \varphi_k\ \left\{\left(\nabla^T\ \underline{\mathbf{D}}\right)^\beta \left(\mathbf{r}^T\ \underline{\mathbf{K}}\right)^\alpha\right\}\left(\ \underline{\mathbf{F}}\ \nabla\right)_\beta \left(\ \underline{\mathbf{G}}\ \nabla\right)_\alpha \tilde{\varphi}_l \quad \equiv \quad \text{- term2} \\
&-\int \mathrm{d}\mathbf{r}\ \frac{1}{r_g}\ \varphi_k\ \left(\mathbf{r}^T\ \underline{\mathbf{K}}\right)^\alpha \left\{\left(\nabla^T\ \underline{\mathbf{D}}\right)^\beta \left(\ \underline{\mathbf{F}}\ \nabla\right)_\beta \left(\ \underline{\mathbf{G}}\ \nabla\right)_\alpha \tilde{\varphi}_l\right\} \quad \equiv \quad \text{- term3.}
\end{aligned}$$

As similar integrals were calculated in our previous works [25, 26], we only show here the final results for term1, term2, and term3.

1. *term1* $\qquad \int \mathrm{d}\mathbf{r}\ \frac{1}{r_g}\ \left\{\left(\nabla^T\ \underline{\mathbf{D}}\right)^\beta \varphi_k\right\}\ \left(\mathbf{r}^T\ \underline{\mathbf{K}}\ \underline{\mathbf{G}}\ \nabla\right)\ \left(\ \underline{\mathbf{F}}\ \nabla\right)_\beta \tilde{\varphi}_l$

$$\begin{aligned}
&\left\{\left(\nabla^T\ \underline{\mathbf{D}}\right)^\beta \varphi_k\right\}\ \left(\mathbf{r}^T\ \underline{\mathbf{K}}\ \underline{\mathbf{G}}\ \nabla\right)\ \left(\ \underline{\mathbf{F}}\ \nabla\right)_\beta \tilde{\varphi}_l = \left\{\underline{\mathbf{D}}_\gamma{}^\beta\ \partial^\gamma\ \varphi_k\right\}\left[\left(\mathbf{r}^T\ \underline{\mathbf{K}}\ \underline{\mathbf{G}}\right)^\alpha\ \underline{\mathbf{F}}_\beta{}^\rho\ \partial_\alpha\partial_\rho\tilde{\varphi}_l\right] = \\
= &\ \varphi_k\Big[\ 4(\mathbf{r}^T\ \underline{\mathbf{K}}\ \underline{\mathbf{G}}\ \tilde{\underline{\mathbf{A}}}_l\ \underline{\mathbf{F}}^T\ \underline{\mathbf{D}}^T\underline{\mathbf{A}}_k\mathbf{r}) - 8\left(\mathbf{r}^T\ \underline{\mathbf{K}}\ \underline{\mathbf{G}}\ \tilde{\underline{\mathbf{A}}}_l\mathbf{r}\right)\left(\mathbf{r}^T\underline{\mathbf{A}}_k\ \underline{\mathbf{D}}\ \underline{\mathbf{F}}\ \tilde{\underline{\mathbf{A}}}_l\mathbf{r}\right) + 4\alpha_l\left(\mathbf{r}^T\ \underline{\mathbf{K}}\ \underline{\mathbf{G}}\ \tilde{\underline{\mathbf{A}}}_l\mathbf{r}\right)\left(\mathbf{r}^T\underline{\mathbf{A}}_k\ \underline{\mathbf{D}}\ \underline{\mathbf{F}}\ \tilde{\mathbf{v}}^l\right) \\
&+4\alpha_l\ \left(\mathbf{r}^T\ \underline{\mathbf{K}}\ \underline{\mathbf{G}}\ \tilde{\mathbf{v}}^l\right)\left(\mathbf{r}^T\underline{\mathbf{A}}_k\ \underline{\mathbf{D}}\ \underline{\mathbf{F}}\ \tilde{\underline{\mathbf{A}}}_l\mathbf{r}\right) - 2\alpha_l^2\ \left(\mathbf{r}^T\ \underline{\mathbf{K}}\ \underline{\mathbf{G}}\ \tilde{\mathbf{v}}^l\right)\left(\mathbf{r}^T\underline{\mathbf{A}}_k\ \underline{\mathbf{D}}\ \underline{\mathbf{F}}\ \tilde{\mathbf{v}}^l\right) + \\
&-2\alpha_k\ \left(\mathbf{r}^T\ \underline{\mathbf{K}}\ \underline{\mathbf{G}}\ \tilde{\underline{\mathbf{A}}}_l\ \underline{\mathbf{F}}^T\ \underline{\mathbf{D}}^T\mathbf{v}^k\right) + 4\alpha_k\ \left(\mathbf{r}^T\ \underline{\mathbf{K}}\ \underline{\mathbf{G}}\ \tilde{\underline{\mathbf{A}}}_l\mathbf{r}\right)\left(\mathbf{v}^{kT}\underline{\mathbf{D}}\ \underline{\mathbf{F}}\ \tilde{\underline{\mathbf{A}}}_l\mathbf{r}\right) - 2\alpha_k\alpha_l\ \left(\mathbf{r}^T\ \underline{\mathbf{K}}\ \underline{\mathbf{G}}\ \tilde{\underline{\mathbf{A}}}_l\mathbf{r}\right)\left(\mathbf{v}^{kT}\ \underline{\mathbf{D}}\ \underline{\mathbf{F}}\ \tilde{\mathbf{v}}^l\right) + \\
&-2\alpha_k\alpha_l\ \left(\mathbf{r}^T\ \underline{\mathbf{K}}\ \underline{\mathbf{G}}\ \tilde{\mathbf{v}}^l\right)\left(\mathbf{v}^{kT}\ \underline{\mathbf{D}}\ \underline{\mathbf{F}}\ \tilde{\underline{\mathbf{A}}}_l\mathbf{r}\right) + \alpha_k\alpha_l^2\ \left(\mathbf{r}^T\ \underline{\mathbf{K}}\ \underline{\mathbf{G}}\ \tilde{\mathbf{v}}^l\right)\left(\mathbf{v}^{kT}\ \underline{\mathbf{D}}\ \underline{\mathbf{F}}\ \tilde{\mathbf{v}}^l\right)\Big]\tilde{\varphi}_l
\end{aligned} \tag{44}$$

where the above transformations (44) can be easily performed using (15) and (18). Hence the final form of the integral is:

$$\begin{aligned}
&\int \mathrm{d}\mathbf{r}\ \frac{1}{r_g}\ \left\{\left(\nabla^T\ \underline{\mathbf{D}}\right)^\beta \phi_k\right\}\ \left(\mathbf{r}^T\ \underline{\mathbf{K}}\ \underline{\mathbf{G}}\ \nabla\right)\ \left(\ \underline{\mathbf{F}}\ \nabla\right)_\beta \tilde{\phi}_l = \\
= &\ \frac{\partial}{\partial\alpha_k}\frac{\partial}{\partial\alpha_l}\int \mathrm{d}\mathbf{r}\ \frac{1}{r_g}\ \left\{\left(\nabla^T\ \underline{\mathbf{D}}\right)^\beta \varphi_k\right\}\ \left(\mathbf{r}^T\ \underline{\mathbf{K}}\ \underline{\mathbf{G}}\ \nabla\right)\ \left(\ \underline{\mathbf{F}}\ \nabla\right)_\beta \tilde{\varphi}_l\Big|_{\alpha_k=\alpha_l=0} = \\
= &\ 4\ \langle\phi_k|\ \frac{1}{r_g}\ (\mathbf{r}^T\ \underline{\mathbf{K}}\ \underline{\mathbf{G}}\ \tilde{\underline{\mathbf{A}}}_l\ (\underline{\mathbf{D}}\ \underline{\mathbf{F}})^T\underline{\mathbf{A}}_k\mathbf{r})\ |\tilde{\phi}_l\rangle - 8\ \langle\phi_k|\ \frac{1}{r_g}\ \left(\mathbf{r}^T\ \underline{\mathbf{K}}\ \underline{\mathbf{G}}\ \tilde{\underline{\mathbf{A}}}_l\mathbf{r}\right)\left(\mathbf{r}^T\underline{\mathbf{A}}_k\ \underline{\mathbf{D}}\ \underline{\mathbf{F}}\ \tilde{\underline{\mathbf{A}}}_l\mathbf{r}\right)\ |\tilde{\phi}_l\rangle + \\
&+4\ \langle\varphi_k|\ \frac{1}{r_g}\ \left(\mathbf{v}^{kT}\mathbf{r}\right)\ \left(\mathbf{r}^T\ \underline{\mathbf{K}}\ \underline{\mathbf{G}}\ \tilde{\underline{\mathbf{A}}}_l\mathbf{r}\right)\left(\mathbf{r}^T\underline{\mathbf{A}}_k\ \underline{\mathbf{D}}\ \underline{\mathbf{F}}\ \tilde{\mathbf{v}}^l\right)\ |\tilde{\varphi}_l\rangle + 4\ \langle\varphi_k|\ \frac{1}{r_g}\ \left(\mathbf{v}^{kT}\mathbf{r}\right)\ \left(\mathbf{r}^T\ \underline{\mathbf{K}}\ \underline{\mathbf{G}}\ \tilde{\mathbf{v}}^l\right)\left(\mathbf{r}^T\underline{\mathbf{A}}_k\ \underline{\mathbf{D}}\ \underline{\mathbf{F}}\ \tilde{\underline{\mathbf{A}}}_l\mathbf{r}\right)\ |\tilde{\varphi}_l\rangle + \\
&-2\ \langle\varphi_k|\ \frac{1}{r_g}\ \left(\mathbf{r}^T\ \underline{\mathbf{K}}\ \underline{\mathbf{G}}\ \tilde{\underline{\mathbf{A}}}_l\ (\underline{\mathbf{D}}\ \underline{\mathbf{F}})^T\mathbf{v}^k\right)\ \left(\tilde{\mathbf{v}}^{lT}\mathbf{r}\right)\ |\tilde{\varphi}_l\rangle + 4\ \langle\varphi_k|\ \frac{1}{r_g}\ \left(\mathbf{r}^T\ \underline{\mathbf{K}}\ \underline{\mathbf{G}}\ \tilde{\underline{\mathbf{A}}}_l\mathbf{r}\right)\left(\mathbf{r}^T\tilde{\underline{\mathbf{A}}}_l\ (\underline{\mathbf{D}}\ \underline{\mathbf{F}})^T\ \mathbf{v}^k\right)\ \left(\tilde{\mathbf{v}}^{lT}\mathbf{r}\right)\ |\tilde{\varphi}_l\rangle + \\
&-2\ \left(\mathbf{v}^{kT}\ \underline{\mathbf{D}}\ \underline{\mathbf{F}}\ \tilde{\mathbf{v}}^l\right)\ \langle\varphi_k|\ \frac{1}{r_g}\ \left(\mathbf{r}^T\ \underline{\mathbf{K}}\ \underline{\mathbf{G}}\ \tilde{\underline{\mathbf{A}}}_l\mathbf{r}\right)\ |\tilde{\varphi}_l\rangle - 2\ \langle\varphi_k|\ \frac{1}{r_g}\ \left(\mathbf{r}^T\ \underline{\mathbf{K}}\ \underline{\mathbf{G}}\ \tilde{\mathbf{v}}^l\right)\left(\mathbf{r}^T\ \tilde{\underline{\mathbf{A}}}_l\ (\underline{\mathbf{D}}\ \underline{\mathbf{F}})^T\mathbf{v}^k\right).
\end{aligned} \tag{45}$$

2. *term 2* $\int \mathrm{d}\mathbf{r}\, \varphi_k \, \frac{1}{r_g} \left\{ \left(\nabla^T \, \underline{\mathbf{D}} \right)^\beta \, \left(\mathbf{r}^T \, \underline{\mathbf{K}} \right)^\alpha \right\} \left(\underline{\mathbf{F}} \, \nabla \right)_\beta \left(\underline{\mathbf{G}} \, \nabla \right)_\alpha \, \tilde{\varphi}_l$

We note that:

$$\left\{ \left(\nabla^T \, \underline{\mathbf{D}} \right)^\beta \, \left(\mathbf{r}^T \, \underline{\mathbf{K}} \right)^\alpha \right\} \left(\underline{\mathbf{F}} \, \nabla \right)_\beta \left(\underline{\mathbf{G}} \, \nabla \right)_\alpha \tilde{\varphi}_l \;=\; \left(\underline{\mathbf{D}} \, \underline{\mathbf{F}} \;\; \nabla \right)_\gamma \left(\underline{\mathbf{K}} \, \underline{\mathbf{G}} \, \nabla \right)^\gamma \tilde{\varphi}_l = \left(\nabla^T \, \underline{\mathbf{G}}^T \, \underline{\mathbf{K}}^T \, \underline{\mathbf{D}} \, \underline{\mathbf{F}} \, \nabla \right) \tilde{\varphi}_l. \tag{46}$$

Hence, the expression (46) is analogous to (43).

3. *term3* $\int \mathrm{d}\mathbf{r}\, \varphi_k \, \frac{1}{r_g} \left(\mathbf{r}^T \, \underline{\mathbf{K}} \right)^\alpha \left\{ \left(\nabla^T \, \underline{\mathbf{D}} \right)^\beta \left(\underline{\mathbf{F}} \, \nabla \right)_\beta \left(\underline{\mathbf{G}} \, \nabla \right)_\alpha \tilde{\varphi}_l \right\}$

First we make a few simple transformations:

$$\left(\mathbf{r}^T \, \underline{\mathbf{K}} \right)^\alpha \left\{ \left(\nabla^T \, \underline{\mathbf{D}} \right)^\beta \left(\underline{\mathbf{F}} \, \nabla \right)_\beta \left(\underline{\mathbf{G}} \, \nabla \right)_\alpha \tilde{\varphi}_l \right\} = \left(\mathbf{r}^T \, \underline{\mathbf{K}} \, \underline{\mathbf{G}} \right)^\alpha \left(\underline{\mathbf{D}} \, \underline{\mathbf{F}} \right)_\rho^{\;\beta} \, \partial^\rho \, \partial_\beta \, \partial_\alpha \, \tilde{\varphi}_l \tag{47}$$

Based on (22) we get:

$$\begin{aligned}
&\int \mathrm{d}\mathbf{r}\, \phi_k \, \frac{1}{r_g} \left(\mathbf{r}^T \, \underline{\mathbf{K}} \right)^\alpha \left\{ \left(\nabla^T \, \underline{\mathbf{D}} \right)^\beta \left(\underline{\mathbf{F}} \, \nabla \right)_\beta \left(\underline{\mathbf{G}} \, \nabla \right)_\alpha \tilde{\phi}_l \right\} = \\
= \;& \frac{\partial}{\partial \alpha_k} \frac{\partial}{\partial \alpha_l} \int \mathrm{d}\mathbf{r}\, \varphi_k \, \frac{1}{r_g} \left(\mathbf{r}^T \, \underline{\mathbf{K}} \right)^\alpha \left\{ \left(\nabla^T \, \underline{\mathbf{D}} \right)^\beta \left(\underline{\mathbf{F}} \, \nabla \right)_\beta \left(\underline{\mathbf{G}} \, \nabla \right)_\alpha \tilde{\varphi}_l \right\} \Big|_{\alpha_k = \alpha_l = 0} = \\
= \;& +4 \, \langle \phi_k \mid \frac{1}{r_g} \left(\mathbf{r}^T \, \underline{\mathbf{K}} \, \underline{\mathbf{G}} \;\; \tilde{\mathbf{A}}_l \, \underline{\mathbf{D}} \, \underline{\mathbf{F}} \, \tilde{\mathbf{A}}_l \mathbf{r} \right) \mid \tilde{\phi}_l \rangle + 12 \;\; \mathrm{Tr} \left[\tilde{A}_l D F \right] \, \langle \phi_k \mid \frac{1}{r_g} \left(\mathbf{r}^T \, \underline{\mathbf{K}} \, \underline{\mathbf{G}} \, \tilde{\mathbf{A}}_l \mathbf{r} \right) \mid \tilde{\phi}_l \rangle + \\
& +4 \, \langle \phi_k \mid \frac{1}{r_g} \left(\mathbf{r}^T \, \underline{\mathbf{K}} \, \underline{\mathbf{G}} \, \tilde{\mathbf{A}}_l \, \mathbf{F}^T \mathbf{D}^T \tilde{\mathbf{A}}_l \mathbf{r} \right) \mid \tilde{\phi}_l \rangle - 8 \, \langle \phi_k \mid \frac{1}{r_g} \left(\mathbf{r}^T \, \underline{\mathbf{K}} \, \underline{\mathbf{G}} \, \tilde{\mathbf{A}}_l \mathbf{r} \right) \left(\mathbf{r}^T \tilde{\mathbf{A}}_l \, \underline{\mathbf{D}} \, \underline{\mathbf{F}} \, \tilde{\mathbf{A}}_l \mathbf{r} \right) \mid \tilde{\phi}_l \rangle + \\
& -2 \, \langle \varphi_k \mid \frac{1}{r_g} \left(\mathbf{v}^{kT} \mathbf{r} \right) \left(\mathbf{r}^T \underline{\mathbf{K}} \, \underline{\mathbf{G}} \, \tilde{\mathbf{A}}_l \, \underline{\mathbf{D}} \, \underline{\mathbf{F}} \, \tilde{\mathbf{v}}^l \right) \mid \tilde{\varphi}_l \rangle - 6 \;\; \mathrm{Tr} \left[\tilde{A}_l D F \right] \, \langle \varphi_k \mid \frac{1}{r_g} \left(\mathbf{v}^{kT} \mathbf{r} \right) \left(\mathbf{r}^T \, \underline{\mathbf{K}} \, \underline{\mathbf{G}} \, \tilde{\mathbf{v}}^l \right) \mid \tilde{\varphi}_l \rangle + \\
& -2 \, \langle \varphi_k \mid \frac{1}{r_g} \left(\mathbf{v}^{kT} \mathbf{r} \right) \left(\mathbf{r}^T \underline{\mathbf{K}} \, \underline{\mathbf{G}} \, \tilde{\mathbf{A}}_l \, (\underline{\mathbf{D}} \, \underline{\mathbf{F}})^T \, \tilde{\mathbf{v}}^l \right) \mid \tilde{\varphi}_l \rangle + 4 \, \langle \varphi_k \mid \frac{1}{r_g} \left(\mathbf{v}^{kT} \mathbf{r} \right) \left(\mathbf{r}^T \, \underline{\mathbf{K}} \, \underline{\mathbf{G}} \, \tilde{\mathbf{A}}_l \mathbf{r} \right) \left(\mathbf{r}^T \tilde{\mathbf{A}}_l \, \underline{\mathbf{D}} \, \underline{\mathbf{F}} \, \tilde{\mathbf{v}}^l \right) \mid \tilde{\varphi}_l \rangle + \\
& +4 \, \langle \varphi_k \mid \frac{1}{r_g} \left(\mathbf{v}^{kT} \mathbf{r} \right) \left(\mathbf{r}^T \, \underline{\mathbf{K}} \, \underline{\mathbf{G}} \, \tilde{\mathbf{v}}^l \right) \left(\mathbf{r}^T \tilde{\mathbf{A}}_l \, \underline{\mathbf{D}} \, \underline{\mathbf{F}} \, \tilde{\mathbf{A}}_l \mathbf{r} \right) \mid \tilde{\varphi}_l \rangle + 4 \, \langle \varphi_k \mid \frac{1}{r_g} \left(\mathbf{v}^{kT} \mathbf{r} \right) \left(\mathbf{r}^T \, \underline{\mathbf{K}} \, \underline{\mathbf{G}} \, \tilde{\mathbf{A}}_l \mathbf{r} \right) \left(\tilde{\mathbf{v}}^{lT} \, \underline{\mathbf{D}} \, \underline{\mathbf{F}} \, \tilde{\mathbf{A}}_l \mathbf{r} \right) \mid \tilde{\varphi}_l \rangle
\end{aligned} \tag{48}$$

X. MATRIX ELEMENTS

The elemental integrals are now evaluated.

A. Overlap integral

$$\begin{aligned}\langle\varphi_k|\tilde{\varphi}_l\rangle &= \frac{\partial}{\partial\alpha_k}\frac{\partial}{\partial\alpha_l}\langle\varphi_k|\tilde{\varphi}_l\rangle\Big|_{\alpha_k,\alpha_l=0} = \\ &= \frac{\pi^{3n/2}}{|\tilde{A}_{kl}|^{3/2}}\,\frac{\partial}{\partial\alpha_k}\frac{\partial}{\partial\alpha_l}\exp\left[\frac{1}{4}(\alpha_k v^k+\alpha_l\tilde{v}^l)^T\tilde{A}_{kl}^{-1}(\alpha_k v^k+\alpha_l\tilde{v}^l)\right]\Big|_{\alpha_k,\alpha_l=0} = \\ &= \frac{\pi^{3n/2}}{2}\frac{v^{kT}\tilde{A}_{kl}^{-1}\tilde{v}^l}{|\tilde{A}_{kl}|^{3/2}}. \end{aligned} \tag{49}$$

The normalized overlap integral is:

$$\begin{aligned}\mathsf{S}_{kl} &\equiv \frac{\langle\phi_k|\tilde{\phi}_l\rangle}{\left(\langle\phi_k|\phi_k\rangle\langle\phi_l|\phi_l\rangle\right)^{1/2}} = \frac{\left(|A_{kk}|^{3/2}|A_{ll}|^{3/2}\right)^{1/2}}{|\tilde{A}_{kl}|^{3/2}}\,\frac{\left(v^{kT}\tilde{A}_{kl}^{-1}\tilde{v}^l\right)}{(v^{kT}A_{kk}^{-1}v^k\,\tilde{v}^{lT}A_{ll}^{-1}\tilde{v}^l)^{1/2}} = \\ &= 2^{3n/2}\left(\frac{\left||L_k|\right|\left||L_l|\right|}{|\tilde{A}_{kl}|}\right)^{3/2}\frac{\left(v^{kT}\tilde{A}_{kl}^{-1}\tilde{v}^l\right)}{(v^{kT}A_{kk}^{-1}v^k\,\tilde{v}^{lT}A_{ll}^{-1}\tilde{v}^l)^{1/2}}. \end{aligned} \tag{50}$$

The details of the derivation were shown in Ref. [24]. Now additional integrals need to be calculated.

B. $\langle\phi_k|\left(\mathbf{r}^T\underline{\mathbf{X}}\mathbf{r}\right)|\tilde{\phi}_l\rangle$

Using the representation of basis functions (3) presented by Eq. (4) and using (13) we get:

$$\begin{aligned}\langle\phi_k|\left(\mathbf{r}^T\underline{\mathbf{X}}\mathbf{r}\right)|\tilde{\phi}_l\rangle &= -\frac{\partial}{\partial\beta}\langle\phi_k|\exp[-\beta\mathbf{r}^T\underline{\mathbf{X}}\mathbf{r}]|\tilde{\phi}_l\rangle\Big|_{\beta=0} = -\frac{\partial}{\partial\beta}\frac{\pi^{3n/2}}{2}\frac{v^{kT}(\tilde{A}_{kl}+\beta X)^{-1}\tilde{v}^l}{|\tilde{A}_{kl}+\beta X|^{3/2}}\Big|_{\beta=0} = \\ &= \langle\phi_k|\tilde{\phi}_l\rangle\left(\frac{3}{2}\,\mathrm{Tr}\,[\tilde{A}_{kl}^{-1}X]+\frac{\left(v^{kT}\tilde{A}_{kl}^{-1}X\tilde{A}_{kl}^{-1}\tilde{v}^l\right)}{\left(v^{kT}\tilde{A}_{kl}^{-1}\tilde{v}^l\right)}\right). \end{aligned} \tag{51}$$

C. $\langle\phi_k|\left(\mathbf{r}^T\underline{\mathbf{X}}\mathbf{r}\right)\left(\mathbf{r}^T\underline{\mathbf{Y}}\mathbf{r}\right)|\tilde{\phi}_l\rangle$

This integral is evaluated in the following way:

$$\begin{aligned}&\left\langle\phi_k\right|\left(\mathbf{r}^T\mathbf{X}\mathbf{r}\right)\left(\mathbf{r}^T\mathbf{Y}\mathbf{r}\right)\left|\tilde{\phi}_l\right\rangle = \\ &= \frac{\partial}{\partial\alpha_k}\frac{\partial}{\partial\alpha_l}\frac{\partial}{\partial\beta}\frac{\partial}{\partial\gamma}\int\mathrm{d}\mathbf{r}\,\exp\left[-\mathbf{r}^T\left(\tilde{\mathbf{A}}_{kl}+\beta\mathbf{X}+\gamma\mathbf{Y}\right)\mathbf{r}+(\alpha_k\mathbf{v}^k+\alpha_l\tilde{\mathbf{v}}^l)^T\mathbf{r}\right]|_{\beta=\gamma=\alpha_k=\alpha_l=0} = \\ &= \pi^{3n/2}\,|\tilde{A}_{kl}|^{-3/2}\frac{\partial}{\partial\beta}\frac{\partial}{\partial\gamma}\,|I+\beta\tilde{A}_{kl}^{-1}X+\gamma\tilde{A}_{kl}^{-1}Y|^{-3/2}\frac{1}{2}\left(v^{kT}\left(\tilde{A}_{kl}+\beta X+\gamma Y\right)^{-1}\tilde{v}^l\right)|_{\beta=\gamma=0}. \end{aligned} \tag{52}$$

Using the general expression for the derivative of a product of a determinant and a scalar both being dependent on the derivative variable and the scalar being a product of a vector, a matrix, and a vector ($v^{kT}W^{-1}v^{l}$) we get:

$$\frac{\partial}{\partial\beta}\frac{\partial}{\partial\gamma}\left\{|M|^{-3/2}\left(v^{kT}W^{-1}v^{l}\right)\right\}|_{\beta=\gamma=0} = \tag{53}$$

$$\begin{aligned} = \; & |M|^{-3/2}\left\{\frac{9}{4}\;\mathrm{Tr}\,[M^{-1}\partial_\beta M]\;\mathrm{Tr}\,[M^{-1}\partial_\gamma M]\left(v^{kT}W^{-1}v^{l}\right)+\frac{3}{2}\;\mathrm{Tr}\,[M^{-1}\partial_\beta M]\left(v^{kT}W^{-1}(\partial_\gamma W)\;W^{-1}v^{l}\right)+\right. \\ & +\frac{3}{2}\;\mathrm{Tr}\,[M^{-1}(\partial_\beta M)M^{-1}\partial_\gamma M]\left(v^{kT}W^{-1}v^{l}\right)+\frac{3}{2}\;\mathrm{Tr}\,[M^{-1}\partial_\gamma M]\left(v^{kT}W^{-1}(\partial_\beta W)W^{-1}v^{l}\right)+ \\ & \left.+\left(v^{kT}W^{-1}(\partial_\beta W)W^{-1}(\partial_\gamma W)\;W^{-1}v^{l}\right)+\left(v^{kT}W^{-1}(\partial_\gamma W)\;W^{-1}(\partial_\beta W)W^{-1}v^{l}\right)\right\}|_{\beta=\gamma=0}. \end{aligned} \tag{54}$$

Using in (54) the following:

$$\begin{aligned} |M| &= |I+\beta\tilde{A}_{kl}^{-1}X+\gamma\tilde{A}_{kl}^{-1}Y|, \qquad M^{-1}=I^{-1}, \\ W^{-1} &= \left(I+\beta\tilde{A}_{kl}^{-1}X+\gamma\tilde{A}_{kl}^{-1}Y\right)^{-1}, \quad W^{-1}=\tilde{A}_{kl}^{-1}, \end{aligned} \tag{55}$$

we get:

$$\begin{aligned} & \left\langle\phi_k\right|\left(\mathbf{r}^T\mathbf{X}\mathbf{r}\right)\left(\mathbf{r}^T\mathbf{Y}\mathbf{r}\right)\left|\tilde{\phi}_l\right\rangle = \\ = \; & \langle\phi_k|\tilde{\phi}_l\rangle\left\{\frac{9}{4}\;\mathrm{Tr}\left[\tilde{A}_{kl}^{-1}X\right]\;\mathrm{Tr}\left[\tilde{A}_{kl}^{-1}Y\right]+\frac{3}{2}\;\mathrm{Tr}\left[\tilde{A}_{kl}^{-1}X\right]\frac{\left(v^{kT}\tilde{A}_{kl}^{-1}Y\;\tilde{A}_{kl}^{-1}v^{l}\right)}{\left(v^{kT}\tilde{A}_{kl}^{-1}v^{l}\right)}+\right. \\ & +\frac{3}{2}\;\mathrm{Tr}\left[\tilde{A}_{kl}^{-1}X\tilde{A}_{kl}^{-1}Y\right]+\frac{3}{2}\;\mathrm{Tr}\left[\tilde{A}_{kl}^{-1}Y\right]\frac{\left(v^{kT}\tilde{A}_{kl}^{-1}X\tilde{A}_{kl}^{-1}v^{l}\right)}{\left(v^{kT}\tilde{A}_{kl}^{-1}v^{l}\right)}+ \\ & \left.+\frac{1}{\left(v^{kT}\tilde{A}_{kl}^{-1}v^{l}\right)}\left(\left(v^{kT}\tilde{A}_{kl}^{-1}X\;\tilde{A}_{kl}^{-1}Y\;\tilde{A}_{kl}^{-1}v^{l}\right)+\left(v^{kT}\tilde{A}_{kl}^{-1}Y\;\tilde{A}_{kl}^{-1}X\;\tilde{A}_{kl}^{-1}v^{l}\right)\right)\right\}. \end{aligned} \tag{56}$$

D. $\langle\varphi_k|\left(\mathbf{v}^{kT}\mathbf{r}\right)\left(\mathbf{r}^T\underline{\mathbf{X}}\tilde{\mathbf{v}}^{l}\right)|\tilde{\varphi}_l\rangle$

This integral is calculated analogically to integral $\langle\phi_k|\left(\mathbf{r}^T\underline{\mathbf{X}}\mathbf{r}\right)|\tilde{\phi}_l\rangle$:

$$\begin{aligned} \langle\varphi_k|\left(\mathbf{v}^{kT}\mathbf{r}\right)\left(\mathbf{r}^T\underline{\mathbf{X}}\tilde{\mathbf{v}}^{l}\right)|\tilde{\varphi}_l\rangle &= \frac{\partial}{\partial\alpha}\frac{\partial}{\partial\beta}\langle\varphi_k|\exp[\alpha\mathbf{v}^{kT}\mathbf{r}+\beta\mathbf{r}^T\underline{\mathbf{X}}\tilde{\mathbf{v}}^{l}]|\tilde{\varphi}_l\rangle\Big|_{\alpha=0,\beta=0} = \\ &= \frac{\pi^{3n/2}}{|\tilde{A}_{kl}|^{3/2}}\frac{1}{4}\left(\tilde{v}^{lT}X^T\tilde{A}_{kl}^{-1}v^{k}+v^{kT}\tilde{A}_{kl}^{-1}X\tilde{v}^{l}\right)=\langle\phi_k|\tilde{\phi}_l\rangle\frac{1}{\left(v^{kT}\tilde{A}_{kl}^{-1}\tilde{v}^{l}\right)}\left(v^{kT}\tilde{A}_{kl}^{-1}X\tilde{v}^{l}\right). \end{aligned} \tag{57}$$

E. $\left\langle\phi_k\left|\frac{1}{r_g}\right|\tilde{\phi}_l\right\rangle$, **where** $g = i \; or \; ij$

$$\left\langle\phi_k\left|\frac{1}{r_g}\right|\tilde{\phi}_l\right\rangle = \frac{2}{\sqrt{\pi}}\frac{\langle\phi_k|\tilde{\phi}_l\rangle}{\mathrm{Tr}\,[\tilde{A}_{kl}^{-1}J_g]^{1/2}}\left\{1-\frac{1}{3}\frac{\left(v^{kT}\tilde{A}_{kl}^{-1}J_g\tilde{A}_{kl}^{-1}\tilde{v}^{l}\right)}{\left(v^{kT}\tilde{A}_{kl}^{-1}\tilde{v}^{l}\right)\;\mathrm{Tr}\,[\tilde{A}_{kl}^{-1}J_g]}\right\}. \tag{58}$$

Details of the derivation of this integral were shown in [24].

F. $\left\langle \phi_k \middle| \frac{1}{r_g} \left(\mathbf{r}^T \underline{\mathbf{X}} \mathbf{r} \right) \middle| \tilde{\phi}_l \right\rangle$

This integral is evaluated as follows:

$$\left\langle \phi_k \middle| \frac{1}{r_g} \left(\mathbf{r}^T \underline{\mathbf{X}} \mathbf{r} \right) \middle| \tilde{\phi}_l \right\rangle = -\frac{\pi^{(3n-1)/2}}{|\tilde{A}_{kl}|^{3/2}} \int_0^\infty \mathrm{d}t \, \frac{\partial}{\partial \beta} \, |I + t^2 \tilde{A}_{kl}^{-1} J_g + \beta \tilde{A}_{kl}^{-1} X|^{-3/2} \left(v^{kT} \left(\tilde{A}_{kl} + t^2 J_g + \beta X \right)^{-1} \tilde{v}^l \right) |_{\beta=0} \,, \tag{59}$$

where

$$|I + t^2 \tilde{A}_{kl}^{-1} J_g + \beta \tilde{A}_{kl}^{-1} X|^{-3/2} \equiv \left(1 + t^2 a + \beta b + t^2 \beta (a \cdot b - c) \right)^{-3/2}, \tag{60}$$

and where $a = \mathrm{Tr}\,[\tilde{A}_{kl}^{-1} J_g]$, $b = \mathrm{Tr}\,[\tilde{A}_{kl}^{-1} X]$, $c = \mathrm{Tr}\,[\tilde{A}_{kl}^{-1} J_g \tilde{A}_{kl}^{-1} X]$.

$$\begin{aligned}
&\frac{\partial}{\partial \beta} \left\{ \left(1 + t^2 a + \beta b + t^2 \beta (a \cdot b - c) \right)^{-3/2} \left(v^{kT} \left(\tilde{A}_{kl} + t^2 J_g + \beta X \right)^{-1} \tilde{v}^l \right) \right\} |_{\beta=0} = \\
&= -(1 + t^2 a)^{-3/2} \left(\frac{3}{2} \, b \, \left(v^{kT} \left(\tilde{A}_{kl} + t^2 J_g \right)^{-1} \tilde{v}^l \right) + \left(v^{kT} \left(\tilde{A}_{kl} + t^2 J_g \right)^{-1} X \left(\tilde{A}_{kl} + t^2 J_g \right)^{-1} \tilde{v}^l \right) \right) \\
&\quad + \frac{3}{2} \, c \, (1 + t^2 a)^{-5/2} \left(v^{kT} \left(\tilde{A}_{kl} + t^2 J_g \right)^{-1} \tilde{v}^l \right) \equiv -\frac{1}{(1 + t^2 a)^{3/2}} w_0 + \frac{t^2}{(1 + t^2 a)^{5/2}} w_2 - \frac{t^4}{(1 + t^2 a)^{7/2}} w_4,
\end{aligned} \tag{61}$$

where

$$w_0 = \frac{3}{2} \, b \, a_1 + c_1, \tag{62}$$

$$w_2 = \frac{3}{2} \, c \, a_1 + \frac{3}{2} \, b \, a_2 + c_2, \tag{63}$$

$$w_4 = \frac{3}{2} \, c \, a_2 + c_3, \tag{64}$$

and

$$a_1 = \left(p^T \tilde{A}_{kl}^{-1} q \right), \tag{65}$$

$$a_2 = \left(p^T \, \tilde{A}_{kl}^{-1} J_g \tilde{A}_{kl}^{-1} \, q \right), \tag{66}$$

$$c_1 = \left(p^T \tilde{A}_{kl}^{-1} X \tilde{A}_{kl}^{-1} q \right), \tag{67}$$

$$c_2 = \left[\left(p^T \tilde{A}_{kl}^{-1} J_g \tilde{A}_{kl}^{-1} X \, \tilde{A}_{kl}^{-1} q \right) + \left(p^T \tilde{A}_{kl}^{-1} X \, \tilde{A}_{kl}^{-1} J_g \tilde{A}_{kl}^{-1} q \right) \right], \tag{68}$$

$$c_3 = \left(p^T \tilde{A}_{kl}^{-1} J_g \tilde{A}_{kl}^{-1} X \, \tilde{A}_{kl}^{-1} J_g \tilde{A}_{kl}^{-1} q \right). \tag{69}$$

So finally:

$$\begin{aligned}
&\left\langle \phi_k \middle| \frac{1}{r_g} \left(\mathbf{r}^T \mathbf{X} \mathbf{r} \right) \middle| \tilde{\phi}_l \right\rangle = \\
&= \frac{2}{\sqrt{\pi}} \frac{\langle \phi_k | \tilde{\phi}_l \rangle}{\left(v^{kT} \tilde{A}_{kl}^{-1} \tilde{v}^l \right)} \frac{1}{\mathrm{Tr}\,[\tilde{A}_{kl}^{-1} J_g]^{1/2}} \left\{ w_0 - \frac{1}{3} \frac{1}{\mathrm{Tr}\,[\tilde{A}_{kl}^{-1} J_g]} \, w_2 + \frac{1}{5} \frac{1}{\mathrm{Tr}\,[\tilde{A}_{kl}^{-1} J_g]^2} \, w_4 \right\}.
\end{aligned} \tag{70}$$

G. $\left\langle \phi_k \middle| \frac{1}{r_g} \left(\mathbf{r}^T \underline{\mathbf{X}} \mathbf{r} \right) \left(\mathbf{r}^T \underline{\mathbf{Y}} \mathbf{r} \right) \middle| \tilde{\phi}_l \right\rangle$

This integral is evaluated as follows:

$$\begin{aligned}
&\left\langle \phi_k \middle| \frac{1}{r_g} \left(\mathbf{r}^T \underline{\mathbf{X}} \mathbf{r} \right) \left(\mathbf{r}^T \underline{\mathbf{Y}} \mathbf{r} \right) \middle| \tilde{\phi}_l \right\rangle = \\
&= \frac{\pi^{(3n-1)/2}}{|\tilde{A}_{kl}|^{3/2}} \int_0^\infty \mathrm{d}t \, \frac{\partial}{\partial \beta} \frac{\partial}{\partial \gamma} \, |I + t^2 \tilde{A}_{kl}^{-1} J_g + \beta \tilde{A}_{kl}^{-1} X + \gamma \tilde{A}_{kl}^{-1} Y|^{-3/2} \left(v^{kT} \left(\tilde{A}_{kl} + t^2 J_g + \beta X + \gamma Y \right)^{-1} \tilde{v}^l \right) |_{\beta=\gamma=0}
\end{aligned} \tag{71}$$

Further calculations are tedious, but analogous to those for integral $\left\langle \phi_k \middle| \left(\mathbf{r}^T \mathbf{X} \mathbf{r} \right) \left(\mathbf{r}^T \mathbf{Y} \mathbf{r} \right) \middle| \tilde{\phi}_l \right\rangle$ and $\left\langle \phi_k \middle| \frac{1}{r_g} \left(\mathbf{r}^T \mathbf{X} \mathbf{r} \right) \middle| \tilde{\phi}_l \right\rangle$

H. $\left\langle\varphi_k\right| \frac{1}{r_g} \left(\mathbf{r}^T \underline{\mathbf{X}} \mathbf{v}^m\right) \left(\mathbf{r}^T \underline{\mathbf{Y}} \mathbf{v}^n\right) \left|\tilde{\varphi}_l\right\rangle$, **where** $m, n = l$ **or** $m, n = k$

This integral is calculated analogously to $\left\langle\phi_k\right|\frac{1}{r_g}\left|\tilde{\phi}_l\right\rangle$ when α_k and α_l are set to zero:

$$\begin{aligned}
&\left\langle\varphi_k\right| \frac{1}{r_g} \left(\mathbf{r}^T \underline{\mathbf{X}} \mathbf{v}^m\right) \left(\mathbf{r}^T \underline{\mathbf{Y}} \mathbf{v}^n\right) \left|\tilde{\varphi}_l\right\rangle = \left\langle\varphi_k\right| \frac{1}{r_g} \left(\underline{\mathbf{X}} \mathbf{v}^m\right)^T \mathbf{r} \left(\underline{\mathbf{Y}} \mathbf{v}^n\right)^T \mathbf{r} \left|\tilde{\varphi}_l\right\rangle = \\
&= \frac{2}{\sqrt{\pi}} \frac{\partial}{\partial\alpha} \frac{\partial}{\partial\beta} \int_0^\infty \mathrm{d}t \int \mathrm{d}\mathbf{r} \exp\left[-\mathbf{r}^T \left(\underline{\tilde{\mathbf{A}}}_{kl} + t^2 \underline{\mathbf{J}}_g\right)\mathbf{r} + \left(\alpha\left(\underline{\mathbf{X}}\mathbf{v}^m\right) + \beta\left(\underline{\mathbf{Y}}\mathbf{v}^n\right)\right)^T \mathbf{r}\right] \,|_{\alpha=\beta=0} = \\
&= \frac{\pi^{3n/2}}{2} \frac{\left(v^{kT} \tilde{A}_{kl}^{-1} v^l\right)}{|\tilde{A}_{kl}|^{3/2}} \frac{2}{\sqrt{\pi}} \frac{1}{\mathrm{Tr}\,[\tilde{A}_{kl}^{-1} J_g]^{1/2} \left(v^{kT} \tilde{A}_{kl}^{-1} v^l\right)} \left[\left(p^T \tilde{A}_{kl}^{-1} q\right) - \frac{1}{3\,\mathrm{Tr}\,[\tilde{A}_{kl}^{-1} J_g]} \left(p^T \tilde{A}_{kl}^{-1} J_g \tilde{A}_{kl}^{-1} q\right)\right], \qquad (72)
\end{aligned}$$

where $a \equiv \mathrm{Tr}\,[\tilde{A}_{kl}^{-1} J_g]$, $(Xv^m) \equiv p$, $(Yv^n) \equiv q$.

I. $\left\langle\varphi_k\right| \frac{1}{r_g} \left(\mathbf{r}^T \underline{\mathbf{X}} \mathbf{r}\right) \left(\mathbf{r}^T \underline{\mathbf{Z}} \mathbf{v}^m\right) \left(\mathbf{r}^T \underline{\mathbf{Y}} \mathbf{v}^n\right) \left|\tilde{\varphi}_l\right\rangle$, **where** $m, n = l$ **or** $m, n = k$

This integral is calculated analogously to integral $\left\langle\phi_k\right|\frac{1}{r_g} \left(\mathbf{r}^T \underline{\mathbf{X}} \mathbf{r}\right)\left|\tilde{\phi}_l\right\rangle$ with α_k and α_l set to zero:

$$\begin{aligned}
&\left\langle\varphi_k\right| \frac{1}{r_g} \left(\mathbf{r}^T \underline{\mathbf{X}} \mathbf{r}\right) \left(\mathbf{r}^T \underline{\mathbf{Z}} \mathbf{v}^m\right) \left(\mathbf{r}^T \underline{\mathbf{Y}} \mathbf{v}^n\right) \left|\tilde{\varphi}_l\right\rangle = -\frac{\partial}{\partial\gamma} \frac{\partial}{\partial\alpha} \frac{\partial}{\partial\beta} \left\langle\varphi_k\right| \frac{1}{r_g} \exp\left[-\gamma \left(\mathbf{r}^T \underline{\mathbf{X}} \mathbf{r}\right) + \left(\alpha \underline{\mathbf{Z}} \mathbf{v}^m + \beta \underline{\mathbf{Y}} \mathbf{v}^n\right)^T \mathbf{r}\right] \left|\tilde{\varphi}_l\right\rangle \,|_{\gamma=\alpha=\beta=0} = \\
&= -\frac{\pi^{(3n-1)/2}}{|\tilde{A}_{kl}|^{3/2}} \frac{\partial}{\partial\gamma} \int_0^\infty \mathrm{d}t \left(1 + t^2 a + \gamma b + t^2 \gamma (a \cdot b - c)\right)^{-3/2} (Zv^m)^T \left(\tilde{A}_{kl} + t^2 J_g + \gamma\, X\right)^{-1} Y v^n \,|_{\gamma=0}, \qquad (73)
\end{aligned}$$

where

$$|I + t^2 \tilde{A}_{kl}^{-1} J_g + \gamma\, \tilde{A}_{kl}^{-1} X|^{-3/2} = \left(1 + t^2 a + \gamma b + t^2 \gamma (a \cdot b - c)\right)^{-3/2} \qquad (74)$$

and $a = \mathrm{Tr}\,[\tilde{A}_{kl}^{-1} J_g]$, $b = \mathrm{Tr}\,[\tilde{A}_{kl}^{-1} X]$, $c = \mathrm{Tr}\,[\tilde{A}_{kl}^{-1} J_g \tilde{A}_{kl}^{-1} X]$, $p = Zv^m$, $q = Yv^n$.

$$\begin{aligned}
&\frac{\partial}{\partial\gamma} \left\{\left(1 + t^2 a + \gamma b + t^2 \gamma (a \cdot b - c)\right)^{-3/2} p^T \left(\tilde{A}_{kl} + t^2 J_g + \gamma\, X\right)^{-1} q\right\} \,|_{\gamma=0} = \\
&= -\frac{1}{(1 + t^2 a)^{3/2}} \left[\frac{3}{2} b \left(p^T \tilde{A}_{kl}^{-1} q\right) + \left(p^T \tilde{A}_{kl}^{-1} X \tilde{A}_{kl}^{-1} q\right)\right] + \\
&+ \frac{t^2}{(1 + t^2 a)^{5/2}} \left[\frac{3}{2} b \left(p^T \tilde{A}_{kl}^{-1} J_g \tilde{A}_{kl}^{-1} q\right) + \frac{3}{2} c \left(p^T \tilde{A}_{kl}^{-1} q\right) + \left(p^T \tilde{A}_{kl}^{-1} J_g \tilde{A}_{kl}^{-1} X \tilde{A}_{kl}^{-1} q\right) + \left(p^T \tilde{A}_{kl}^{-1} X \tilde{A}_{kl}^{-1} J_g \tilde{A}_{kl}^{-1} q\right)\right] + \\
&- \frac{t^4}{(1 + t^2 a)^{7/2}} \left[\frac{3}{2} c \left(p^T \tilde{A}_{kl}^{-1} J_g \tilde{A}_{kl}^{-1} q\right) + \left(p^T \tilde{A}_{kl}^{-1} J_g \tilde{A}_{kl}^{-1} X \tilde{A}_{kl}^{-1} J_g \tilde{A}_{kl}^{-1} q\right)\right] \\
&\equiv -\frac{1}{(1 + t^2 a)^{3/2}} w_0 + \frac{t^2}{(1 + t^2 a)^{5/2}} w_2 - \frac{t^4}{(1 + t^2 a)^{7/2}} w_4, \qquad (75)
\end{aligned}$$

where

$$\begin{aligned}
w_0 &= \frac{3}{2} b \left(p^T \tilde{A}_{kl}^{-1} q\right) + \left(p^T \tilde{A}_{kl}^{-1} X \tilde{A}_{kl}^{-1} q\right), \qquad (76) \\
w_2 &= \frac{3}{2} b \left(p^T \tilde{A}_{kl}^{-1} J_g \tilde{A}_{kl}^{-1} q\right) + \frac{3}{2} c \left(p^T \tilde{A}_{kl}^{-1} q\right) + \left(p^T \tilde{A}_{kl}^{-1} J_g \tilde{A}_{kl}^{-1} X \tilde{A}_{kl}^{-1} q\right) + \left(p^T \tilde{A}_{kl}^{-1} X \tilde{A}_{kl}^{-1} J_g \tilde{A}_{kl}^{-1} q\right) \\
w_4 &= \frac{3}{2} c \left(p^T \tilde{A}_{kl}^{-1} J_g \tilde{A}_{kl}^{-1} q\right) + \left(p^T \tilde{A}_{kl}^{-1} J_g \tilde{A}_{kl}^{-1} X \tilde{A}_{kl}^{-1} J_g \tilde{A}_{kl}^{-1} q\right). \qquad (77)
\end{aligned}$$

Finally

$$\left\langle \varphi_k \right| \frac{1}{r_g} \left(\mathbf{r}^T \underline{\mathbf{X}} \mathbf{r}\right) \left(\mathbf{r}^T \underline{\mathbf{Z}} \mathbf{v}^m\right) \left(\mathbf{r}^T \underline{\mathbf{Y}} \mathbf{v}^n\right) \left| \tilde{\varphi}_l \right\rangle =$$

$$= \frac{2}{\sqrt{\pi}} \frac{\langle \varphi_k | \tilde{\varphi}_l \rangle}{\left(v^{kT} \tilde{A}_{kl}^{-1} \tilde{v}^l\right)} \frac{1}{\mathrm{Tr}\,[\tilde{A}_{kl}^{-1} J_g]^{1/2}} \left\{ w_0 - \frac{1}{3} \frac{1}{\mathrm{Tr}\,[\tilde{A}_{kl}^{-1} J_g]}\, w_2 + \frac{1}{5} \frac{1}{\mathrm{Tr}\,[\tilde{A}_{kl}^{-1} J_g]^2}\, w_4 \right\}. \tag{78}$$

XI. COMPUTATIONAL IMPLEMENTATION AND TEST CALCULATIONS

Algorithms for the leading relativistic corrections (mv, dar, oo, and ss) for the singlet P states derived in this work are implemented on a parallel computer platform using Frotran90 and MPI (message passing interface). The implementation is general and can be applied to atoms with an arbitrary number of electrons.

The test calculations are performed for the lowest ten ^1P states of the helium atom and for the lowest four ^1P states of the beryllium atom. These systems are chosen because results for some of the states considered here were calculate before by Drake and Yan [27] and by Puchalski *et al.* [7]. This enables comparison and verification of the present algorithms.

The results for the helium atoms are presented in Table I. The INM and FNM total non-relativistic energies and the corresponding mv, dar, oo, and ss relativistic corrections are shown. The INM results are compared with the results of Drake and Yan [27]. Three basis sets are used in the calculations for each state. For all states the basis sets include 800, 1000, and 1200. The INM total energies obtained by Drake and Yan are either equal or slightly lower than ours. For higher states, where the energies of Drake and Yan are more noticeably lower than our energies. Including more ECGs would be necessary to achieve better agreement of the two sets of results. For the ground state, where our non-relativistic energy agrees with the energy of Drake and Yan to twelve significant figures, the agreement between our and their values of the relativistic corrections is also very good. It is also very good for the first and second excited states where our nonrelativistic energies are virtually the same as theirs. For the nineth state, where our total energy agrees with the energy of Drake and Yan to nine digits, the difference in the mv and dar corrections appear in the fourth digit, and in the oo correction in the sixth digit.

It is interesting to compare the results obtained for the top 11^1P state of ^4He with the corresponding results for $^4He^+$. For $^4He^+$ with 25 Gaussians in the basis set the total energy and the mv, dar, and oo corrections are -1.999725850786, -9.9930591, 7.9951921, and $0.2192592_{10^{-2}}$ a.u., respectively. The corresponding values for $^\infty He^+$ are: -1.999999999913, -9.9985399, 7.998480420, and 0 a.u.. The comparison is interesting because, as the helium atom becomes excited to increasingly higher Rydberg states, the system starts to resemble the He^+ ion and a free electron. Thus, non-relativistic total energy, as well as the corrections, should converge to the values obtained for He^+ (with both finite and infinite nuclear masses). This indeed happens. It is particularly interesting to examine the INM and FNM oo corrections for He^+. The INM result is zero because the terms proportional to the inverse of the nuclear mass vanish and the two-electron term is not present. It is also not present in the FNM result, but the terms proportional to the inverse of the nuclear mass are not zero. They represent the interaction of the orbital momentum of the electron with the orbital momentum of the moving nucleus. Also, as one can see by examining the oo FNM results in Table I, the ^4He n^1P results converge with increasing n to the 1^2S $^4He^+$ result (given above), as they should. In conclusion, the above analysis of the results for the helium atom lends confidence that the algorithms derived and implemented in this work are likely correct.

The next set of tests are performed for the lowest four ^1P states of the beryllium atom. The INM and FNM results obtained in the calculations with 9500, 11000, and 12500 ECGs are presented in Table II. As one can see, the total energy for all four states is converged to 10-11 digits with the number of the basis functions. The convergence of the mv and dar corrections, and, in particular, the oo corrections is also very good. The results for the lowest ^1P state (the only state calculated before) are compared with the results of Puchalski *et al.* [7]. It should be noted that the "drachmanization" procedure (extrapolation/regularization procedure) was applied in their calculations thus the results for the mv and dar corrections were not directly obtained as expectation values of the corresponding operators, as they have been in our calculations. As one can see, our mv and dar INM corrections converge very well to their results. Also, our oo correction agrees with theirs within five significant digits.

Finally, the last set of results (shown in Table III) concerns the $n^1P \rightarrow (n+1)^1P$ transition energies for the beryllium atom and their comparison with the experimental date [28]. In the table the transition energies are calculated using the results from Table II obtained with 12500 ECGs. The values obtained at the non-relativistic INM level, the non-relativistic FNM level, and the FNM+rel level are shown in the table. For the lowest $2^1P \rightarrow 3^1P$ transition, going from the non-relativistic INM result to the non-relativistic FNM result lowest the transition-energy value by about 1.5 cm^{-1}. Further lowering by more than 2 cm^{-1} is due to including the relativistic corrections. The most complete

results of 17621.780 cm^{-1} obtained at the FNM+rel level differs from the experiment by only 0.21 cm^{-1}. For the other two transitions, $3^1P \rightarrow 4^1P$ and $4^1P \rightarrow 5^1P$, the calculated values are even closer to the experiment (0.15 and 0.10 cm^{-1}, respectively). The difference is likely due to not including the QED corrections in the present calulations.

XII. SUMMARY

In summary, algorithms for calculating the leading relativistic corrections for singlet P bound states of small atoms have been derived and implemented. All-electron explicitly correlated Gaussian functions are used in expanding the non-relativistic INM and FNM wave functions of the system. The wave functions are used to calculate the expectation values of the mv, dar, oo, and ss relativistic operators. These operators are obtained by transforming the laboratory-frame operators representing both the nucleus and the electrons into operators expressed in terms of the internal coordinates. With that the effect of the finite nuclear mass is explicitly included in the relativistic corrections and does not need to be added as a perturbation. Such an approach also eliminates the need of separately determining the relativistic recoil effects.

Test calculations are performed for some lowest lying P states of the helium and beryllium atoms. The results are compared with literature values obtained in calculations and with the experimental results. The results for the 3^1P, 4^1P, and 5^1P states of the Be atom are the first ever high-accuracy values presented for these states.

The next step in this project will involve implementation of the leading quantum electrodynamics (QED) corrections for the P states. The spin-orbit relativistic corrections will also be implemented to perform calculations spin states higher than singlet. This will be followed by application calculations of the P spectra of the Be and B atoms, and of the B^+ and C^+ atomic ions.

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TABLE I: Helium atom. The convergence of the total nonrelativistic energies, the expectation values of delta-functions, and the leading relativistic corrections with the number of basis functions for the lowest ten ^1P excited states. All values are given in a.u.

State		Basis	$\langle\hat{H}_{nr}\rangle$	$\langle\delta(\mathbf{r}_1)\rangle$	$\langle\delta(\mathbf{r}_{12})\rangle\times10^4$	$\langle\hat{H}_{mv}\rangle$	$\langle\hat{H}_{d}\rangle$	$\langle\hat{H}_{oo}\rangle\times10^2$	$\langle\hat{H}_{ss}\rangle\times10^3$
$2\,^1P$	^{4}He	800	-2.123545654114	1.2738542	7.3457900	-10.0236617	8.0015543	-2.2539634	4.6154960
	^{4}He	1000	-2.123545654122	1.2738551	7.3444226	-10.0236647	8.0015604	-2.2539634	4.6146368
	^{4}He	1200	-2.123545654125	1.2738674	7.3444465	-10.0237540	8.0016373	-2.2539633	4.6146518
	^{3}He	1200	-2.123448345016	1.2736977	7.3419103	-10.0219675	8.0005723	-2.3262136	4.6130583
	$^\infty$He	1200	-2.123843086496	1.2743859	7.3522038	-10.0292159	8.0048933	-2.0330474	4.6195259
	$^\infty$He	[27]	-2.123843086498092(8)	1.274392886(1)	7.351691(3)	-10.029251357(5)	8.004937054	-2.03304741(2)	
$3\,^1P$	^{4}He	800	-2.054862661145	1.2731024	2.5177494	-10.0058893	7.9983476	-0.8896287	1.5819486
	^{4}He	1000	-2.054862661147	1.2731027	2.5177572	-10.0058816	7.9983493	-0.8896287	1.5819535
	^{4}He	1200	-2.054862661148	1.2731027	2.5176958	-10.0058816	7.9983493	-0.8896287	1.5819149
	^{3}He	1200	-2.054769843454	1.2729319	2.5168768	-10.0040897	7.9972764	-0.9615442	1.5814003
	$^\infty$He	1200	-2.055146362092	1.2736248	2.5202006	-10.0113599	8.0016291	-0.6697369	1.5834887
	$^\infty$He	[27]	-2.05514636209195(3)	1.273627296(1)	2.520151(6)	-10.011372887(6)	8.001644581	-0.669736894(7)	
$4\,^1P$	^{4}He	800	-2.030790385838	1.2728701	1.1136996	-9.9997559	7.9973287	-0.5113823	0.6997581
	^{4}He	1000	-2.030790385839	1.2728758	1.1136413	-9.9997941	7.9973646	-0.5113822	0.6997215
	^{4}He	1200	-2.030790385841	1.2728764	1.1136196	-9.9997943	7.9973683	-0.5113822	0.6997078
	^{3}He	1200	-2.030699019258	1.2727053	1.1132674	-9.9980016	7.9962936	-0.5831875	0.6994865
	$^\infty$He	1200	-2.031069650450	1.2733993	1.1146967	-10.0052750	8.0006536	-0.2918278	0.7003846
	$^\infty$He	[27]	-2.03106965045024(3)	1.2734058005(6)	1.114645(6)	-10.005316142(5)		-0.291827835(6)	
$5\,^1P$	^{4}He	800	-2.019628669868	1.2727879	0.5826951	-9.9973160	7.9969792	-0.3710273	0.3661181
	^{4}He	1000	-2.019628669872	1.2727942	0.5826911	-9.9973578	7.9970189	-0.3710273	0.3661156
	^{4}He	1200	-2.019628669875	1.2727952	0.5826607	-9.9973570	7.9970252	-0.3710272	0.3660965
	^{3}He	1200	-2.019537939367	1.2726241	0.5824793	-9.9955642	7.9959498	-0.4427882	0.3659826
	$^\infty$He	1200	-2.019905989900	1.2733184	0.5832154	-10.0028384	8.0003125	-0.1516084	0.3664451
	$^\infty$He	[27]	-2.01990598990083(2)	1.2733249851(1)	0.583173(3)	-10.0028777129(6)		-0.151608431(6)	
$6\,^1P$	^{4}He	800	-2.013557677123	1.2727421	0.3412714	-9.9961052	7.9967672	-0.3077908	0.2144271
	^{4}He	1000	-2.013557677128	1.2727517	0.3411935	-9.9961545	7.9968277	-0.3077907	0.2143782
	^{4}He	1200	-2.013557677130	1.2727573	0.3411921	-9.9961918	7.9968625	-0.3077907	0.2143773
	^{3}He	1200	-2.013467279447	1.2725861	0.3410870	-9.9943989	7.9957869	-0.3795307	0.2143113
	$^\infty$He	1200	-2.013833979671	1.2732806	0.3415137	-10.0016734	8.0001507	-0.0884360	0.2145794
	$^\infty$He	[27]	-2.01383397967174(2)	1.2732890481O(3)	0.3414934(3)	-10.0017251175(3)		-0.0884359852(3)	
$7\,^1P$	^{4}He	800	-2.009893609042	1.2727137	0.2165311	-9.9954896	7.9966281	-0.2752843	0.1360505
	^{4}He	1000	-2.009893609065	1.2727272	0.2164759	-9.9955113	7.9967128	-0.2752839	0.1360158
	^{4}He	1200	-2.009893609072	1.2727277	0.2164378	-9.9955122	7.9967158	-0.2752837	0.1359919
	^{3}He	1200	-2.009803406698	1.2725565	0.2163717	-9.9937192	7.9956401	-0.3470126	0.1359503
	$^\infty$He	1200	-2.010169314526	1.2732511	0.2166402	-10.0009939	8.0000044	-0.0559629	0.1361191
	$^\infty$He	[27]	-2.01016931452935(2)	1.2732707343(3)	0.2166053(1)	-10.001113216(2)		-0.05596288972(3)	
$8\,^1P$	^{4}He	800	-2.007513801107	1.2726407	0.1458046	-9.9947009	7.9961916	-0.2569171	0.0916117
	^{4}He	1000	-2.007513801243	1.2726841	0.1458006	-9.9949443	7.9964640	-0.2569160	0.0916092
	^{4}He	1200	-2.007513801284	1.2727071	0.1457329	-9.9951065	7.9966088	-0.2569148	0.0915667
	^{3}He	1200	-2.007423723079	1.2725359	0.1456910	-9.9933136	7.9955330	-0.3286380	0.0915404
	$^\infty$He	1200	-2.007789127103	1.2732305	0.1458612	-10.0005882	7.9998976	-0.0376117	0.0916473
	$^\infty$He	[27]	-2.00778912713322(2)	1.2732604446(3)	0.1457990(3)	-10.000750251(2)		-0.0376116535(8)	
$9\,^1P$	^{4}He	800	-2.005881313840	1.2725353	0.1029647	-9.9939087	7.9955430	-0.2457698	0.0646946
	^{4}He	1000	-2.005881314641	1.2725861	0.1028061	-9.9942233	7.9958620	-0.2457689	0.0645949
	^{4}He	1200	-2.005881314827	1.2726513	0.1027757	-9.9946361	7.9962720	-0.2457671	0.0645759
	^{3}He	1200	-2.005791320403	1.2724801	0.1027475	-9.9928433	7.9951962	-0.3174865	0.0645582
	$^\infty$He	1200	-2.006156384506	1.2731748	0.1028619	-10.0001172	7.9995606	-0.0264756	0.0646301
	$^\infty$He	[27]	-2.00615638465286(5)	1.2732542261(2)	0.1027385(3)	-10.000540617(1)		-0.0264755498(5)	
$10\,^1P$	^{4}He	800	-2.004713084479	1.2721804	0.0755772	-9.9923789	7.9933213	-0.2386266	0.0474866
	^{4}He	1000	-2.004713090035	1.2724376	0.0753410	-9.9936184	7.9949378	-0.2386216	0.0473382
	^{4}He	1200	-2.004713092853	1.2724796	0.0751998	-9.9938568	7.9952017	-0.2386182	0.0472494
	^{3}He	1200	-2.004623157571	1.2723084	0.0751823	-9.9920642	7.9941261	-0.3103356	0.0472384
	$^\infty$He	1200	-2.004987981689	1.2730030	0.0752532	-9.9993375	7.9984902	-0.0193326	0.0472830
	$^\infty$He	[27]	-2.00498798380222(4)	1.2732502491(2)	0.075076(1)	-10.000398414(1)		-0.019332591(2)	
$11\,^1P$	^{4}He	800	-2.003848396241	1.2719795	0.0572607	-9.9913523	7.9920649	-0.2338431	0.0359780
	^{4}He	1000	-2.003848412311	1.2721844	0.0569009	-9.9930260	7.9933525	-0.2338376	0.0357519
	^{4}He	1200	-2.003848424448	1.2723565	0.0566745	-9.9934859	7.9944338	-0.2338307	0.0356097
	^{3}He	1200	-2.003758532396	1.2721853	0.0566717	-9.9916942	7.9933584	-0.3055488	0.0356079
	$^\infty$He	1200	-2.004123180978	1.2728797	0.0566831	-9.9989639	7.9977212	-0.0145433	0.0356150

TABLE II: Beryllium atom. The convergence of the total nonrelativistic energies, expectation values of delta-functions, and leading relativistic corrections with the number of basis functions for the lowest four ^1P excited states. All values are given in a.u.

State		Basis	$\langle\hat{H}_{nr}\rangle$	$\langle\delta(\mathbf{r}_1)\rangle$	$\langle\delta(\mathbf{r}_{12})\rangle$	$\langle\hat{H}_{mv}\rangle$	$\langle\hat{H}_{d}\rangle$	$\langle\hat{H}_{oo}\rangle$	$\langle\hat{H}_{ss}\rangle$
$2\,^1P$	^{9}Be	9500	-14.472543745	8.722321	0.261305	-266.58448	214.29035	-0.8382247	9.850966
	^{9}Be	11000	-14.472543750	8.722423	0.261303	-266.58700	214.29296	-0.8382247	9.850898
	^{9}Be	12500	-14.472543754	8.722597	0.261301	-266.59220	214.29737	-0.8382247	9.850804
	$^\infty$Be	12500	-14.473451382	8.724225	0.261345	-266.65862	214.33745	-0.8120914	9.852475
	$^\infty$Be	[7]	-14.47345137(4)	8.7244787(2)	0.26132393(7)	-266.66514(2)		-0.8120929(3)	
$3\,^1P$	^{9}Be	9500	-14.392242865	8.747192	0.262268	-267.37477	214.89728	-0.8820805	9.887266
	^{9}Be	11000	-14.392242872	8.747341	0.262267	-267.37866	214.90104	-0.8820804	9.887241
	^{9}Be	12500	-14.392242876	8.747404	0.262267	-267.38043	214.90263	-0.8820804	9.887227
	$^\infty$Be	12500	-14.393143530	8.749025	0.262311	-267.44668	214.94253	-0.8558113	9.888883
$4\,^1P$	^{9}Be	9500	-14.361037776	8.762808	0.262962	-267.87692	215.27667	-0.9135497	9.913425
	^{9}Be	11000	-14.361037784	8.762842	0.262959	-267.87758	215.27759	-0.9135497	9.913310
	^{9}Be	12500	-14.361037790	8.762880	0.262958	-267.87788	215.27856	-0.9135497	9.913293
	$^\infty$Be	12500	-14.361938390	8.764497	0.263002	-267.94406	215.31837	-0.8872040	9.914942
$5\,^1P$	^{9}Be	9500	-14.346975824	8.768325	0.263217	-268.05502	215.41052	-0.9249324	9.923061
	^{9}Be	11000	-14.346975837	8.768433	0.263198	-268.05792	215.41361	-0.9249322	9.922326
	^{9}Be	12500	-14.346975845	8.768442	0.263198	-268.05783	215.41383	-0.9249322	9.922319
	$^\infty$Be	12500	-14.347876276	8.770059	0.263241	-268.12402	215.45363	-0.8985612	9.923968

TABLE III: Beryllium atom. Three lowest $n^1P \to (n+1)^1P$ transition energies calculated using the INM non-relativistic energies, the FNM non-relativistic energies, and the FNM energies that include the relativistic and relativistic corrections. The transition energies are compared with the experimentally derived values from Ref. [28]. All transitions are given in cm^{-1}.

Transition	Basis	$\Delta E_{nr}(^\infty\text{Be})$	$\Delta E_{nr}(^9\text{Be})$	$\Delta E_{nr+rel}(^9\text{Be})$	Experiment
$2^1P \to 3^1P$	9500	17625.537	17624.006	17621.775	
	11000	17625.536	17624.006	17621.772	
	12500	17625.536	17624.005	17621.780	
					17621.99
$3^1P \to 4^1P$	9500	6848.737	6848.726	6847.229	
	11000	6848.737	6848.725	6847.232	
	12500	6848.737	6848.725	6847.241	
					6847.36
$4^1P \to 5^1P$	9500	3086.279	3086.242	3085.704	
	11000	3086.278	3086.241	3085.695	
	12500	3086.277	3086.240	3085.690	
					3085.79