Analytical treatment to Helium isoelectronic ions via Green function expansion of Coulomb interactions: perturbation calculations of ground-state energies with Hydrogenic orbitals

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Inseparability of Coulomb interactions into generic coordinates calls hues of dichotomy in solving Schrödinger equation of multi-electron quantum systems. Especially, Hydrogenic systems have both bound and scattered (ionized) states to achieve completeness relation of respective Hilbert space. Consequently, variational and perturbation calculations experience non-trivial Coulomb (exchange) integrals. Albeit, Born-Oppenheimer approximation simplifies the hamiltonian for electrons of atoms under frozen nuclei, the electrostatic Green function expansion of interactions becomes inevitable prospect. Each pole of Green function expansion is composed of operators of two electrons as a composite of source and test charges. Non-relativistic quantum equations of the source and the test electrons are solved in Whittaker-*M* function and Associated Laguerre polynomial forms respectively. It furnishes all operators of the above mentioned expansions a template of lower and upper incomplete Gamma functions with integer arguments for interior integrals and finally terminable, exact, finitely summed and easily calculable Lauricella functions in exterior integrals in analytical treatment of Coulomb correlations. However, exchange of coordinates among test and source electrons leading to identical integrals ensures symmetric nature of Green function expansion. As a benchmark, we have calculated ground state energies of *He* and isoelectronic ions through perturbation calculations of first, second and higher orders with bound states only. It clearly shows that percentage contribution upto second order perturbation calculation of bound excited states increases with increasing nuclear charge (atomic number, Z) of isoelectronic series. The theoretical development also ensures unquestionable future for analytical treatment of size-extended quantum systems.

Keywords: Helium isoelectronic ions, Coulomb interactions, Green's function expansion, Hydrogenic bound states, first and second order perturbation calculations.

1. Introduction

Interaction among multi-charges of quantum systems has become a fathomless challenge in twenty first century. Dialectical proposals from various schools of state-of-art have come to the fore of science with an appeal for unification[1–6]. In this arena, both the hydrogenic and the oscillator systems have vastly been employed to study complex phenomena[7,8]. In the year of 1929, first landmark contribution of estimating the ground state energy of *He* atom was made by Hylleraas[1]. He intuitively proposed a correlated wavefunction, composed of six parameters giving an excellent variational result. However, it was insignificant to satisfy the cusps condition for three or more particles at coalescence region[9]. In this regard, Bartlett[4] and others suggested inclusion of logarithmic form in wavefunction which was further deployed by Pekeris[5].

He numerically calculated the ground-state energy of *He* atom. Scherr *et al.* and Silverman elegantly performed perturbation calculations of Z^{-1} expansion upto $E_0^{(13)}$ computationally by utilizing wavefunction of Hylleraas[2,3,10]. Later, Bhattacharyya *et al.* conferred an analytical approach with 3-parameter based correlated wavefunction for examining *He* atom[11]. Nakatsuji and cowokers' monumental work of computation on *He* isoelectronic series by Free ICI (Iterative complement interaction) method with scaled Schrödinger equation (SSE) encountered difficulties for large atoms and molecules (number of electrons, *N* >2)[12]. Later on, Nakatsuji *et al.* developed ICI LSE (Local Schrödinger equation) method for calculation of systems upto *N* = 5, algorithm of which is under construction for high performance computation[13]. Other efforts like inclusion of Kinoshita-type expansion, quantum

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Monte-Carlo calculations, many-body perturbation theory (MBPT), Hartree Fock Self Consistent Field and *etc.* improvised moderately accurate results of two-electron systems with high computational cost[14–17]. But all these methodologies extemporize implicit accountability of Coulomb interaction for *He* isoelectronic ions. Recently, Hazra *et al.* represented an elite formalism for Coulomb interactions of 2-D and 3-D *N-e* harmonically confined quantum dots that paved a way to elucidate Hydrogenic sytems[18–22]. In this context, we have constructed exact theoretical development for generic coordinates of individual particles to solve Schrödinger equation of *He* and its iso-electronic species using Green function expansion that circumvents all computation cost and assumptions. We have achieved exact first order energy correction (1.25 a.u.) of *He*-atom and second order perturbation calculation with both singly excited ($1sn_2s$) and doubly excited (n_1sn_2s) bound states analytically, discussed in detail (Section 2 and Section 3).

2. Novel theoretical development

Hamiltonian of a *H*-like *N-e* systems can be written as:-

$$H = \frac{P_n^2}{2M} + \sum_{i=1}^{N} \left\{ \frac{p_i^2}{2m_e} - \frac{Ze^2}{4\pi\in_0\in|\vec{R}-\vec{r}_i|} + \frac{1}{4\pi\in_0\in}\frac{1}{2}\sum_{j\neq i}^{N}\frac{e^2}{\overrightarrow{r_{ij}}} \right\} \quad (1)$$

where Z, M, m_e, $\in$ are the charge of nucleus, mass of nucleus, mass of electron and dielectric constant of medium respectively. Born-Oppenheimer approximation reduces the above Hamiltonian to:

$$H = \sum_{i=1}^{N} \underbrace{\left\{ \frac{p_i^2}{2m_e} - \frac{Ze^2}{4\pi\in_0\in|\vec{r}_i|} \right\}}_{H_i^0} + \underbrace{\frac{1}{4\pi\in_0\in}\frac{1}{2}\sum_{i=1}^{N}\sum_{j\neq i}^{N}\overbrace{\frac{e^2}{\overrightarrow{r_{ij}}}}^{H'_{ij}}}_{H'} \quad (2)$$

Each interaction term (H'_{ij}) can be opened by free electrostatic Green's function multipole expansion[23].

$$\frac{1}{r_{ij}} = \sum_{l=0}^{\infty}\sum_{m=-l}^{+l}\frac{4\pi}{2l+1}\frac{r_<^l}{r_>^{l+1}}Y_l^m(\theta_i,\phi_i)Y_l^{m*}(\theta_j,\phi_j)$$

$$= 4\pi\left[\frac{1}{r_>} + \frac{r_<}{3r_>^2}\left\{Y_1^1(\theta_i,\phi_i)Y_1^{1*}(\theta_j,\phi_j)\right.\right.$$

$$\left.\left. + Y_1^0(\theta_i,\phi_i)Y_1^{0*}(\theta_j,\phi_j) + Y_1^{-1}(\theta_i,\phi_i)Y_1^{-1*}(\theta_j,\phi_j)\right\}\right.$$

$$\left. + \sum_{l=2}^{\infty}\sum_{m=-l}^{+l}\cdots\right] \quad (3)$$

The unperturbed hamiltonian $H^0\xi(r, \theta, \phi) = E^0\xi(r, \theta, \phi)$ for *i*-th particle of *H*-like system (spherical polar coordinates) can be represented as:

$$\left\{-\frac{1}{2}\left[r^{-2}\left(\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}\right) - \frac{L^2}{r^2}\right] - \frac{Z}{r}\right\}\xi(r, \theta, \phi) = E^0\xi(r, \theta, \phi) \quad (4)$$

The solution with spherical harmonics, $\xi^0(r, \theta, \phi) = u(r)Y_l^m(\theta, \phi)$, $m = 0, \pm1, \pm2,..$ where $u(r)$ is a radial part and $Y_l^m(\theta, \phi) = \sqrt{\frac{(2l+1)(l-|m|)!}{4\pi(l-|m|)!}}\ P_l^{|m|}(\cos\theta)e^{im\phi}$ is the angular part.

The radial Schrödinger equation can be represented as:

$$\left\{r^{-2}\left(\frac{d}{dr}r^2\frac{d}{dr}\right) - \frac{l(l+1)}{r^2} + \frac{\beta'}{r} - \frac{\alpha^2}{4}\right\}u(r) = 0 \quad (5)$$

where, $\alpha^2 = -8E^0$ for bound states $E^0 < 0$, $u(r) \longrightarrow 0$ as $r \longrightarrow \infty$, $u(r)$ is finite at $r = 0$ and and $\beta' = 2Z$. $z = \alpha r$ simplifies the above equation, with $u(r) \Rightarrow U(z)$:

$$\left\{\left(\frac{d^2}{dz^2} + \frac{2}{z}\frac{d}{dz}\right) + \frac{\beta}{z} - \frac{l(l+1)}{z^2} - \frac{1}{4}\right\}U(z) = 0 \quad (6)$$

where $\beta = \beta'/\alpha$ and $U(z) = z^{-1}M(z)$ results in:

$$M''(z) + \left\{\frac{\beta}{z} - \frac{l(l+1)}{z^2} - \frac{1}{4}\right\}M(z) = 0 \quad (7)$$

where $M(z)$ is Whittaker-*M* function and $\beta = 2Z\sqrt{-\frac{1}{8E^0}}$.

Comparing with self-adjoint differential equation of Whittaker-*M* function[24] yields the energy and the corresponding bound-state as $E^0 = -\frac{Z^2}{2n^2}$ and $\xi^0(r, \theta, \phi) = N(\alpha r)^{-1}M_{\kappa,\nu}(\alpha r)Y_l^m(\theta, \phi)$ respectively where n is an integer,

$$N = \sqrt{\alpha^3\left(\frac{(n+l)!}{2n(n-l-1)!(2l+1)!^2}\right)}, \quad \alpha = \frac{2Z}{n}, \quad \kappa = n \text{ and } l+1/2 = $$

ν. Naively, [eq. (7)] can be also compared with Associated Laguerre differential equation giving rise to eigenfunction,

$$\xi^0(r, \theta, \phi) = \mathfrak{B}e^{\frac{-\alpha r}{2}}(\alpha r)^l L_{\mathcal{N}}^{2l+1}(\alpha r)Y_l^m(\theta, \phi), \text{ where } \mathcal{N} = n-l-1,$$

n is principal quantum number and $\mathfrak{B} = \sqrt{\alpha^3\left(\dfrac{(nl-1)!}{2n(n+l)!}\right)}$.

The higher order perturbation calculations can be expressed as[25]:

$$E_P = \underbrace{E_P^0}_{\langle \xi_P^0|H_i^0|\xi_P^0 \rangle} + \underbrace{H_{PP}^{(1)}}_{\underset{\langle \xi_P^0|H'_{ij}|\xi_P^0 \rangle}{E_P^{(1)}}} + \overbrace{\sum_{q \neq P} \underbrace{\dfrac{H_{Pq}^{(1)}H_{qP}^{(1)}}{E_P^0 - E_q^0}}_{\dfrac{\langle \xi_P^0|H'_{ij}|\xi_q^0 \rangle\langle \xi_q^0|H'_{ij}|\xi_P^0 \rangle}{E_P^0 - E_q^0}}}^{E_P^{(2)}} + ...(8)$$

where first term is unperturbed energy of the system, second term is the first order, third term is the second order energy corrections and so on.

The Ground-state perturbation calculations ($P=0$, $E_P = E_0 = E_g$) need to evaluate $H_{Pq}^{(1)}$ integral. This integral reduces to $H_{PP}^{(1)}$ when $P = q$ for first order correction. For, $l = 0$ amd $m = 0$, integral can be written as:

$$H_{Pq}^{(1)} = \left\langle \Xi(R, \Theta, \Phi)_P \left| \dfrac{1}{r_>} \right| \Xi(R, \Theta, \Phi)_q \right\rangle \tag{9}$$

where $\Xi(R, \Theta, \Phi) = \prod_{i=1}^{N} \xi^0(r_i, \theta_i, \phi_i)$. Solving radial part for ground-state *He* iso-electronic ions for individual *i*-th, *j*-th spaces as follows where, for bra-space coordinates $\alpha_1 = \alpha_2 = 2Z$ and for ket-space we can have same or different α subject to singly excited or doubly excited states:

$$I = \left\langle \xi(\alpha_1 r_i)\xi(\alpha_2 r_j) \left| \dfrac{1}{r_>} \right| \xi(\alpha'_1 r_i)\xi(\alpha'_2 r_j) \right\rangle \tag{10}$$

Factorizing the integral, for each r_i considering integral over r_j and consequent integration over r_i:

$$\int_0^\infty \xi(\alpha_1 r_i)\xi(\alpha'_1 r_i)\left[\overbrace{\int_0^{r_i}\dfrac{\xi(\alpha_2 r_j)\xi(\alpha'_2 r_j)r_j^2 dr_j}{r_i}}^{I_1}\right.$$
$$\left. + \underbrace{\int_{r_i}^\infty \dfrac{\xi(\alpha_2 r_j)\xi(\alpha'_2 r_j)r_j^2 dr_j}{r_j}}_{I_2}\right]r_i^2 dr_i \tag{11}$$

I_1 and I_2 can be written using normalized associated Laguerre wavefunction, letting $z_j = \alpha_2 r_j$, $w = \dfrac{\alpha'_2}{\alpha_2}$ and employing [eqs. (18)-(19)] shapes the integral to:

Interior enclosure of source electron:

$$I_1 = \dfrac{\mathfrak{B}_2\mathfrak{B}'_2}{\alpha_2^3 r_i}\sum_{k=0}^{n'_2-1}(-1)^k\dfrac{n'_2!(k+2)w^k g^{k+3}}{(n'_2-1-k)!k!}\left(1-e^{-b}\sum_{s=0}^{k+2}\dfrac{b^s}{s!}\right) \tag{12}$$

Exterior enclosure of source electron:

$$I_2 = \dfrac{\mathfrak{B}_2\mathfrak{B}'_2}{\alpha_2^2}\sum_{k=0}^{n'_2-1}(-1)^k\dfrac{n'_2!w^k g^{k+2}(k+1)}{(n'_2-1-k)!(k+1)!}\left(e^{-b}\sum_{s=0}^{k+1}\dfrac{b^s}{s!}\right) \tag{13}$$

where $b = \left(\dfrac{w+1}{2}\alpha_2 r_j\right)$ and $g = \dfrac{2}{w+1}$ respectively. Substituting back in [eq. (11)] and taking $\xi(\alpha_1 r_i)$ and $\xi(\alpha'_1 r_i)$ in Whittaker-*M* function and $\alpha_1 r_i = z_i$, the integral become ($l_1 = l_2$ and $m_1 = m_2$):

$$I = I_s + I_g$$

$$I_s = \dfrac{N_1 N'_1 \mathfrak{B}_2\mathfrak{B}'_2}{\alpha_2^3}\sum_{k=0}^{n'_2-1}(-1)^k w^k g^{k+3}(k+1)(k+2)\binom{n'_2}{(k+1)}$$

$$\times\left[\underbrace{\dfrac{1}{\alpha_1^2 \upsilon}\left\langle M_{k_1,v_1}(z_i)\left|\dfrac{1}{z_i}\right|M_{k_2,v_2}(\upsilon z_i)\right\rangle - \sum_{s=0}^{k+2}\dfrac{1}{s!}\left(\dfrac{1}{g}\right)^s\dfrac{1}{\alpha_1^2 \upsilon}}_{I_{s_a}}\right.$$

$$\left.\times\underbrace{\left\langle M_{k_1,v_1}(z_i)\left|e^{-\left(\frac{w+1}{2}z_i\right)}z_i^{s-1}\right|M_{k_2,v_2}(\upsilon z_i)\right\rangle}_{I_{s_b}}\right] \tag{14}$$

$$I_g = \dfrac{N_1 N'_1 \mathfrak{B}_2\mathfrak{B}'_2}{\alpha_2^2}\sum_{k=0}^{n'_2-1}(-1)^k w^k g^{k+2}(k+1)\binom{n'_2}{(k+1)}\left[\sum_{s=0}^{k+1}\dfrac{1}{s!}\right.$$

$$\left.\times\left(\dfrac{1}{g}\right)^s\dfrac{1}{\alpha_1^3 \upsilon}\underbrace{\left\langle M_{k_1,v_1}(z_i)\left|e^{-\left(\frac{w+1}{2}z_i\right)}z_i^s\right|M_{k_2,v_2}(\upsilon z_i)\right\rangle}_{I_{g_a}}\right] \tag{15}$$

where $\upsilon = \dfrac{\alpha'_1}{\alpha_1}$.

Standard Integral I[26]:

$$\int_0^\infty x^{(\varrho-1)} e^{-bx} M_{\kappa_1,\gamma_1-\frac{1}{2}}(a_1 x) M_{\kappa_2,\gamma_2-\frac{1}{2}}(a_2 x)\,dx = a_1^{\gamma_1} a_2^{\gamma_2}(b+A)^{-\varrho-M}\Gamma(\varrho+M)F_2\left(\varrho+M;\gamma_1-\kappa_1,\gamma_2-\kappa_2;2\gamma_1,2\gamma_2;\dfrac{a_1}{b+A},\dfrac{a_2}{b+A}\right)$$

(16)

where $Re(\varrho + M) > 0$, $Re\left(b \pm \dfrac{1}{2}a_1 \pm \dfrac{1}{2}a_2\right) > 0$ and $M = \gamma_1 + \gamma_2$

Standard Integral II[27]:

$$\int_0^\infty x^{(\sigma-1)} e^{-bx} L_{k_1}^{\mu_1}(a_1 x) L_{k_2}^{\mu_2}(a_2 x)\,dx = (-1)^{(k_1+k_2)}\binom{-(\mu_1+1)}{k_1}\binom{-(\mu_2+1)}{k_2}b^{-\sigma}\Gamma(\sigma)F_2\left(\sigma;-k_1,-k_2;\mu_1+1,\mu_2+1;\dfrac{a_1}{b},\dfrac{a_2}{b}\right)$$

(17)

where $Re(\sigma) > 0$, $Re(b) > 0$

Associated Laguerre polynomial[24]

$$L_k^\mu(x) = \sum_{m=0}^{k}(-1)^m \frac{(\mu+k)!}{(k-m)!(\mu+m)!m!}x^m \qquad \mu > -1$$

(18)

Lower and upper incomplete gamma function[24]:

$$\gamma(a,x) = \int_0^x e^{-t}t^{a-1}dt = (a-1)!\left(1-e^{-x}\sum_{s=0}^{a-1}\frac{x^s}{s!}\right);\ \Gamma(a,x) = \int_x^\infty e^{-t}t^{a-1}dt = (a-1)!\left(e^{-x}\sum_{s=0}^{a-1}\frac{x^s}{s!}\right)$$

(19)

where, $Re(a) > 0$

F_2 to F_1 relation[28].

$$F_2\left(\begin{array}{c}a,b,b'\\c,c'\end{array};d,d'\right) = \sum_{k=0}^{\infty}\frac{(a)_k (b)_k d^k}{(c)_k k!}\,_2F_1\left(\begin{array}{c}b',a+k\\c'\end{array};d'\right)$$

(20)

Chu-Vandermonde identity[29], satisfying conditions: $Re(c') \geq$ and $d' = 1$:

$$_2F_1\left(\begin{array}{c}-b',a+k\\c'\end{array};d'\right) = \frac{(c'-(a+k))_{b'}}{(c')_{b'}}$$

(21)

Solving I_{s_a} using the standard integral [eq. (16)] result in following finite double summed form, where $b = 0$, $a_1 = 1$, $a_2 = \upsilon$, $A = \dfrac{1}{2}(a_1 + a_2)$, $b + A = \dfrac{\upsilon+1}{2}$, $\gamma_1 - \dfrac{1}{2} = l_1 + \dfrac{1}{2}$, $\gamma_2 - \dfrac{1}{2} = l_2 + \dfrac{1}{2}$, $M = \gamma_1 + \gamma_2 = l_1 + l_2 + 2$, $\varrho = 0$, $2v = 0, 1, 2, ..; k-v-1/2 = 1, 2, ..$:

$$I_{s_a} = \upsilon^{(l_2+1)}\left(\frac{\upsilon+1}{2}\right)^{-(l_1+l_2+2)}\Gamma(l_1+l_2+2)$$

$$\times \sum_{p=0}^{\mathcal{N}_1}\sum_{q=0}^{\mathcal{N}_2}\frac{(l_1+l_2+2)_{p+q}(-\mathcal{N}_1)_p(-\mathcal{N}_2)_q}{(2l_1+2)_p(2l_2+2)_q\,p!q!}$$

$$\times\left(\frac{2}{\upsilon+1}\right)^p\left(\frac{2\upsilon}{\upsilon+1}\right)^q$$

(22)

For I_{s_b}, $b = \dfrac{w+1}{2}$, $a_1 = 1$, $a_2 = \upsilon$, $A = \dfrac{1}{2}(a_1 + a_2)$, $b + A = \left(\dfrac{\upsilon+w}{2}+1\right)$, $\gamma_1 - \dfrac{1}{2} = l_1 + \dfrac{1}{2}$, $\gamma_2 - \dfrac{1}{2} = l_2 + \dfrac{1}{2}$, $M = \gamma_1 + \gamma_2$

$= l_1 + l_2 + 2, \varrho = s:$

$$I_{s_b} = \upsilon^{(l_2+1)} \left(\frac{\upsilon + w}{2} + 1 \right)^{-(l_1+l_2+s+2)} \Gamma(l_1 + l_2 + s + 2)$$

$$\times \sum_{p=0}^{\mathcal{N}_1} \sum_{q=0}^{\mathcal{N}_2} \frac{(l_1 + l_2 + s + 2)_{p+q} (-\mathcal{N}_1)_p (-\mathcal{N}_2)_q}{(2l_1+2)_p (2l_2+2)_q \, p! q!}$$

$$\times \left(\frac{2}{\upsilon + w + 2} \right)^p \left(\frac{2\upsilon}{\upsilon + w + 2} \right)^q \tag{23}$$

And similarly for I_{g_a} exploiting the standard integral (eq. (16)) we obtain following simplified form:

$$I_{g_a} = \upsilon^{(l_2+1)} \left(\frac{\upsilon + w}{2} + 1 \right)^{-(l_1+l_2+s+3)} \Gamma(l_1 + l_2 + s + 3)$$

$$\times \sum_{p=0}^{\mathcal{N}_1} \sum_{q=0}^{\mathcal{N}_2} \frac{(l_1 + l_2 + s + 3)_{p+q} (-\mathcal{N}_1)_p (-\mathcal{N}_2)_q}{(2l_1+2)_p (2l_2+2)_q \, p! q!}$$

$$\times \left(\frac{2}{\upsilon + w + 2} \right)^p \left(\frac{2\upsilon}{\upsilon + w + 2} \right)^q \tag{24}$$

where $b = \dfrac{w+1}{2}$, $a_1 = 1$, $a_2 = \upsilon$, $A = (a_1 + a_2)$, $b + A =$

$\left(\dfrac{\upsilon + w}{2} + 1 \right)$, $\gamma_1 - \dfrac{1}{2} = l_1 + \dfrac{1}{2}$, $\gamma_2 - \dfrac{1}{2} = l_2 + \dfrac{1}{2}$, $M = \gamma_1 + \gamma_2$ $= l_1 + l_2 + 2$, $\varrho = s + 1$. Substituting back the [eqs. (22)-(24)] in [eqs. (14), (15)] for $l_1 = l_2 = 0$ we get:

$$I_s = \mathscr{D} \sum_{k=0}^{n_2'-1} (-1)^k w^k g^{k+3} (k+1)(k+2) \binom{n_2'}{k+1} \left\{ \left(\frac{\upsilon+1}{2} \right)^{-2} \right.$$

$$\times \Gamma(2) \sum_{p=0}^{\mathcal{N}_1} \sum_{q=0}^{\mathcal{N}_2} \frac{(2)_{p+q} (-\mathcal{N}_1)_p (-\mathcal{N}_2)_q}{(2)_p (2)_q \, p! q!} \left(\frac{2}{\upsilon+1} \right)^p \left(\frac{2\upsilon}{\upsilon+1} \right)^q$$

$$- \sum_{s=0}^{k+2} \frac{1}{s!} \left(\frac{1}{g} \right)^s \left(\frac{v+w}{2} + 1 \right)^{-(s+2)} \Gamma(s+2) \sum_{p=0}^{\mathcal{N}_1} \sum_{q=0}^{\mathcal{N}_2} \frac{(s+2)_{p+q}}{(2)_p (2)_q}$$

$$\times \frac{(-\mathcal{N}_1)_p (-\mathcal{N}_2)_q}{p! q!} \left(\frac{2}{\upsilon + w + 2} \right)^p \left(\frac{2\upsilon}{\upsilon + w + 2} \right)^q \right\} \tag{25}$$

and

$$I_g = \mathscr{D} \left\{ \sum_{k=0}^{n_2'-1} (-1)^k w^k g^{k+2} (k+1) \binom{n_2'}{k+1} \sum_{s=0}^{k+1} \frac{1}{s!} \left(\frac{1}{g} \right)^s \right.$$

$$\times \left(\frac{v+w}{2} + 1 \right)^{-(s+3)} \Gamma(s+3) \sum_{p=0}^{\mathcal{N}_1} \sum_{q=0}^{\mathcal{N}_2} \frac{(s+3)_{p+q}}{(2)_p (2)_q}$$

$$\times \frac{(-\mathcal{N}_1)_p (-\mathcal{N}_2)_q}{p! q!} \left(\frac{2}{\upsilon + w + 2} \right)^p \left(\frac{2\upsilon}{\upsilon + w + 2} \right)^q \right\} \tag{26}$$

where $\mathscr{D} = \dfrac{N_1 N_2 B\, B\,_2}{\alpha_1^5}$. Adding [eqs. (25), (26)] gives the exact value of the integral [eq. (10)]. I_{s_a}, I_{s_b} and I_{g_a} can also be evaluated using [eq. (17)] yielding same result.

2.1. First order energy correction $E_0^{(1)}$

First order energy correction of the ground-state with $(1s(1)1s(2))$ for isoelectronic Helium ions, the integral in [eq. (10)] attains following diagonal form $(\alpha_1 = \alpha'_1 = \alpha'_2 = 2Z)$:

$$I = \left\langle \xi(\alpha_1 r_i) \xi(\alpha_1 r_j) \left| \frac{1}{r_>} \right| \xi(\alpha_1 r_i) \xi(\alpha_1 r_j) \right\rangle \tag{27}$$

I_s and I_g can be recast as single summed form by employing

$$I_s = \mathscr{D} \sum_{k=0}^{n_2'-1} (-1)^k (k+1)(k+2) \binom{n_2'}{k+1} \left\{ \Gamma(2) \right.$$

$$\times \sum_{p=0}^{\mathcal{N}_1} \frac{(2)_p (-\mathcal{N}_1)_p (-p)_{\mathcal{N}_2}}{(2)_p (2)_{\mathcal{N}_2} \, p!}$$

$$- \sum_{s=0}^{k+2} \frac{1}{s!} (2)^{-(s+2)} \Gamma(s+2)$$

$$\times \sum_{p=0}^{\mathcal{N}_1} \frac{(s+2)_p (-\mathcal{N}_1)_p (-(s+p))_{\mathcal{N}_2}}{(2)_p (2)_{\mathcal{N}_2} \, p!} \right\} \tag{28}$$

and

$$I_g = \mathscr{D} \left\{ \sum_{k=0}^{n_2'-1} (-1)^k (k+1) \binom{n_2'}{k+1} \right.$$

$$\times \sum_{s=0}^{k+1} \frac{1}{s!} (2)^{-(s+3)} \Gamma(s+3)$$

$$\times \left. \sum_{p=0}^{\mathscr{N}_1} \frac{(s+3)_p (-\mathscr{N}_1)_p (-(s+p+1))_{\mathscr{N}_2}}{(2)_p (2)_{\mathscr{N}_2} p!} \right\} \quad (29)$$

Giving the following values $I = I_s + I_g$:

$$I = \left[\frac{5}{32} + \frac{5}{32} \right] \alpha_1$$

$$= \frac{5}{16} \alpha_1$$

$$= \frac{5}{8} Z$$

2.2. Second order energy correction $E^{(2)}_0$

Second order energy correction of ground-states for Helium iso-electronic ions can be represented as:

$$E_0^{(2)} = \sum_{q \neq 0} \frac{H_{0q}^{(1)} H_{q0}^{(1)}}{E_0^{(0)} - E_q^{(0)}} = \sum_{q \neq 0} \frac{\overbrace{\langle \xi_0^0 | H'_{ij} | \xi_q^0 \rangle}^{I_1} \overbrace{\langle \xi_q^0 | H'_{ij} | \xi_0^0 \rangle}^{I_2}}{E_0^{(0)} - E_q^{(0)}} \quad (31)$$

where $E_0^{(0)}$ and $E_q^{(0)}$ are energies of the ground and q-th excited bound states respectively of He isoelectronic ions respectively.

$$I_1 = \left\langle \xi(\alpha_1 r_i) \xi(\alpha_1 r_j) \left| \frac{1}{r_>} \right| \xi(\alpha'_1 r_i) \xi(\alpha'_2 r_j) \right\rangle$$

$$I_2 = \left\langle \xi(\alpha'_1 r_i) \xi(\alpha'_2 r_j) \left| \frac{1}{r_>} \right| \xi(\alpha_1 r_i) \xi(\alpha_1 r_j) \right\rangle \quad (32)$$

Above two integrals can be evaluated similarly as [Eq.(10)] giving end results as [eqs. (25), (26)] and it can then be substituted in [eq. (31)] yielding second order energy.

3. Results and discussion

We have evaluated the ground-state energies of Helium isoelectronic ions (H^-, He, Li^+, Be^{2+}, B^{3+}, C^{4+}, N^{5+}, O^{6+}, F^{7+} and Ne^{8+}) with exact estimation of their first order ($E^{(1)}_0$) and second order ($E^{(2)}_0$) energy correction terms using Green's function expansion of Coulomb interactions for bound states with $l = 0$, $m = 0$ and $n = 1$–100. The unperturbed wave-

functions of bound states are in the parameter free form of generic coordinates of individual particles. Table 1 summaries the values of $E^{(1)}_0$, $E^{(2)}_0$ and ground-state energies (E_g) for different Z (Hydride ion to Ne^{8+}) [Fig. 1(b)]. The obtained ground-state energies are compared with the experimental results[30]. We have also estimated both the % contributions of singly and doubly excited bound states to second order energy correction of Helium atom and residual contributions due to ionized states, relativistic effect and nonadiabatic transition, discussed in detail in next section.

3.1. Analysis of $E^{(1)}_0$ contribution

We have completely determined exact values of first order energy correction for different Z [eq. (30)] catalogued in Table I which matches to literature[30].

3.2. Analysis of $E^{(2)}_0$ contribution

Table 1 and Fig. 1(a) show the quantitative contribution of singly and doubly excited bound states ($l = 0$ and $m = 0$) to second order perturbation energy ($E^{(2)}_0$). As n increases $E^{(2)}_0$ value decreases and reaches zero very sharply within $n = 100$. Singly excited bound states show more quantitative participation than doubly excited bound states. From the Table 1, it is clearly seen that second order correction ($E^{(2)}_0$) is independent of increasing Z unlike $E^{(1)}_0$ but the total %-difference to that of experimental value decreases with increasing Z. For Helium atom ($Z = 2$), the stepping stone to enter into the world of many-body physics, our analytical result shows only 3.25% difference to that of the experimental value. It arises as continuum hydrogenic states are not accounted that significantly contribute to second order energy correction[3]. Complete basis set for hydrogenic system comprises of both bound and continuum states for evaluation of the exact ground-state energy[31]. Scherr conjectured that bound states ($l = 0$ and $m = 0$) contribute 40%, singly ionized and doubly ionized states contribute 40.8% and 10.8% respectively to second order correction without thorough calculations[3]. Although the order of accuracy achieved by Nakatsuji et al. and other computational groups deserves very high esteem, we have chosen inclusion of distinctive phenomena like bound and scattered states, relativistic quantum effect and non-adiabatic transitions analytically[3,12,13]. In this paper, incorporation of bound excited states only for second order perturbation correction exhibits ~3.25% difference of

residual contribution for remaining phenomena. Our analytical results being in agreement with Scherr's results can be easily applicable to size extended systems:

$$E_{exp} - \left[E_0^{(0)} + E_0^{(1)} \right] = \overbrace{-0.15378}^{\text{Predicted total } E_0^{(2)} \text{contribution}}$$

$$E_0^{(2)} \text{ contribution of bound states} = \underbrace{-0.059351016}_{\text{(our analytical result)}}$$

$$\text{Percentage contribution} = \left| \frac{-0.0593510}{-0.15378} \right| \times 100 \sim 39\%$$

The formalism corroborating exact two-center integrals also enlightens the way for multi-configuration variational and perturbation calculations[21].

Symmetry of Green function expansion:

Reciprocity of Green's function is very significant property as it is a two variable function $(\vec{r}_1, \vec{r}_2)$. Epistemology of Bhaskara-II and Kerala School of Mathematics on differential geometry and calculus respectively, greatly helps us visualizing the intricate symmetry details of Green function expansion of Coulomb interaction without going through ex-

Table 1. Comparison of ground-state energies (E_g) of H⁻ to Ne⁸⁺ in a.u. obtained by our analytical treatment with experimental values[30]. Contribution of first order $E_0^{(1)}$ and second order $E_0^{(2)}$) energy correction to ground-state energies for different Z is shown. Values of singly and double excited bound states of $E_0^{(2)}$ for Helium is also given. (Residual contribution $(R_c)\% = \left| \dfrac{E_g - E_{exp}}{E_{exp}} \right| \times 100$

| Z	$E_0^{(0)}$ (a.u.)	$E_0^{(1)}$ (a.u.)	$E_0^{(2)}$ (a.u.)		Eg (a.u.)	Eexp (a.u.)	| R_c% |
1 (H)	-2.0	0.625	$E_0^{(2)}$Total: -0.059351016762180		-0.434351016762179	−0.52776	17.69
2 (He)	-4.0	1.25	**Singly excited bound states**	**Doubly excited bound states**	-2.809351016762170	−2.90378	3.25
			n_1=1s n_2=2s -0.021291525326358	n_1=2s n_2=2s -0.000160569721443			
			n_1=1s n_2=3s -0.004347974700000	n_1=3s n_2=3s -0.000001357868314			
			n_1=1s n_2=4s -0.001625895879581	n_1=4s n_2=4s -0.000000080814105			
			n_1=1s n_2=5s -0.000788420649888	n_1=5s n_2=5s -0.000000010332783			
			n_1=1s n_2=6s -0.000443152057806	n_1=6s n_2=6s -0.000000002023212			
			n_1=1s n_2=7s -0.000274240288945	n_1=7s n_2=7s -0.000000000521487			
			n_1=1s n_2=8s -0.000181658666483	n_1=8s n_2=8s -0.000000000163018			
			n_1=1s n_2=9s -0.000126604502112	n_1=9s n_2=9s -0.000000000058806			
			n_1=1s n_2=10s -0.000091787934680	n_1=10s n_2=10s -0.000000000023696			
			.....	......			
			n_1=1s n_2=100s -0.0000000896	n_1=100s n_2=100s -0.000000000000			
			$E_0^{(2)}$Total: -0.059351016762180				
3 (Li⁺)	-9.0	1.875	$E_0^{(2)}$Total: -0.059351016762180		-7.184351016762	−7.28041	1.31
4 (Be²⁺)	-16.0	2.5	$E_0^{(2)}$Total: -0.059351016762180		-13.559351016762	−13.65744	0.7
5 (B³⁺)	-25.00	3.125	$E_0^{(2)}$Total: -0.059351016762180		-21.934351016762	−22.03603	0.46
6 (C⁴⁺)	-36.0	3.75	$E_0^{(2)}$Total: -0.059351016762180		-32.309351016762	−32.41733	0.33
7 (N⁵⁺)	-49.0	4.375	$E_0^{(2)}$Total: -0.059351016762180		-44.684351016762	−44.80351	0.26
8 (O⁶⁺)	-64.0	5.0	$E_0^{(2)}$Total: -0.059351016762180		-59.059351016762	−59.19580	0.23
9 (F′⁺)	-81.00	5.625	$E_0^{(2)}$Total: -0.059351016762180		-75.434351016762	−75.59658	0.21
10 (Ne⁸⁺)	-100.0	6.25	$E_0^{(2)}$Total: -0.059351016762180		-93.809351016762	−94.00835	0.21
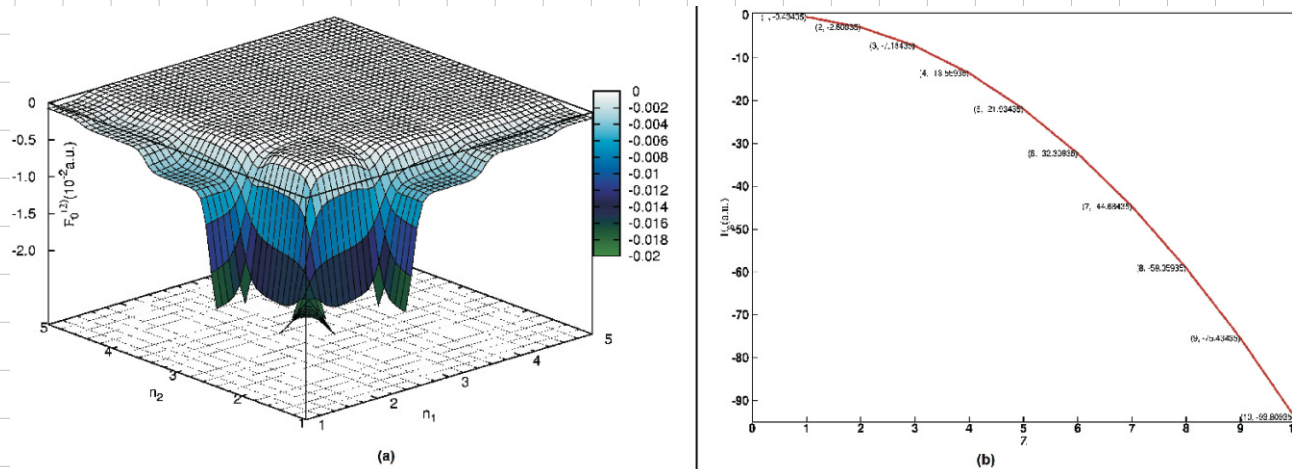
Fig. 1. (a) Contribution of singly (1s(1)ns(2)) and doubly excited bound states (n1s(1)n2s(2)) to second order energy correction ($E_0^{(2)}$) of helium atom (Z=2, n=1 to 5) and (b) Ground-State energies (E_g) vs Atomic number(Z).

plicit mathematics [Fig. 1(a)][32,33]. A cursory glance on bisection of $E_0^{(2)}$-plot along principal quantum numbers unambiguously exhibits mirror image symmetry. It signifies that exchange of two-electron coordinates leads to the same contribution [Fig. 1(a)].

Limitations of multipole expansion in generic co-ordinates:

In our first attempt to solve H-like systems we treated coulomb interactions in terms of integrals of multipole expansions through generic co-ordinates of electrons (order of the pole, $'\mathcal{P}'$). Correlation integrals of all poles ($\mathcal{P} \geq 0$) were also chartered as cumulative products of coulomb-, dipole- and inverse-square-type integrals in finite summed Lauricella functions without coming across the question of divergence alike recent analytical treatment to coulomb interaction of oscillator under magnetic field[20–22]. We obtained ground-state energy of $He \simeq -2.5$ a.u. that includes monopole term (1.5 a.u.) and dipole term contributions ($\simeq 0.0$ a.u.) for all bound states ($l = 0$, $m = 0$). We found no further increment in the result despite of enlarging basis-span. The reason for this failure is that the surface integrals of both Dirichlet and Neumann forms of Coulomb interaction in Green's function expansion decay slowly for Hydrogenic systems and therefore multipole expansion does not merges to the potential form of generic coordinates[32]. On the contrary, as Gaussian form of orbitals decays very fast, both the surface integrals of Dirichlet and Neumann Green function expansions exhibit

sharp falls that virtually leads to well known multi-pole expansion in generic co-ordinates of electrons[22]. In that respect, Green's function can only be used as potential precursor to treat Coulomb interactions of generic coordinates.

4. Conclusion

We have represented a novel theoretical development to estimate the ground-state energies of *He*-isoelectronic ions by employing free electrostatic Green's function expansion for Coulomb interactions upto second order perturbation calculations for all bound states. This analytical route embraces exact evaluation of the first ($E_0^{(1)}$) and the second order ($E_0^{(2)}$) energy correction terms and eliminates the paradox that occurs due to different scaling factors (α) for excited states in higher order perturbation and variational calculations. Moreover, the unperturbed wavefunction is free from correlated form and it incorporates generic coordinates of individual particles unlike the wavefunctions adapted by previous theories a century ago. We have achieved a finest overlap of our analytical result with the experimental values. Subsequently, the difference in values of the two appears because contributions from ionized states are not taken into account. At this juncture, detail and exact investigation of the ground-states with above said due contributions, non-adiabatic transitions and relativistic effect has become in-

exorable fate but it goes beyond the scope of the article. However, this methodology is not only restricted to small systems but also applicable to size extended various quantum systems as it preserves reciprocity and boundary conditions (Dirichlet and Neumann) for Green's function expansion of Coulomb interactions.

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