

Boundary conditions for many-electron systems*

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It is shown that natural boundary conditions for non-relativistic wave functions are of periodic or of homogeneous Robin type. Using theory of singular differential equations and asymptotic central symmetry of Hamiltonian the many-electron wave function is expanded in series both in the vicinity of Coulomb singularities and at infinity. Hydrogenic angular dependence of three leading terms of expansion about Coulomb singularities is found. Exact first and second order cusp conditions are obtained demonstrating redundancy of spherical average in Kato's cusp condition. A confluent hypergeometric series defining arbitrarily high order cusp conditions for the spherically averaged Hamiltonian is presented. Homogeneous Robin boundary conditions are obtained for aperiodic many-electron systems from the expansions. Use of our explicit boundary conditions improves both speed and accuracy of numerical calculations.

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I. INTRODUCTION

Boundary conditions play important role in eigenvalue problems of mathematical physics even if they are imposed implicitly. Explicit use of boundary conditions is crucial in numerical calculations. Before beginning our investigation let us summarize some basic properties of eigenvalue problems. Boundary conditions for eigenvalue equations are obeyed only by eigenfunctions. Differential equations arising from variational principles are always self-adjoint. Eigenfunctions of self-adjoint differential operators satisfy homogeneous boundary conditions. In order to obtain physically acceptable eigenfunctions some regularity conditions should be imposed as well.

Role of regularity and boundary conditions in *existence* of quantum mechanical eigenvalue problems was first recognized by E. Schrödinger [1] and J. von Neumann [2]. These conditions are not always specified explicitly since they can be enforced by substantially weaker conditions imposed on the variational problem [2]. In the first formulation of H atom, the requirement of vanishing variance of current flux was used as a constraint which was changed to the weaker normalization condition by an addendum [3]. Latter form is more conventional mathematically since it is compatible with Sturm-Liouville theory of eigenvalue equations, where $\int |\psi|^2 dv$ represents the denominator of Rayleigh quotient. Von Neumann has concluded that normalization condition for the wave function and requirement of self-adjointness of the Hamiltonian is equivalent to imposing both boundary and regularity conditions on the wave function [2].

In fact, these conditions are too weak to enforce unique regular solutions of Schrödinger equation. Normalization condition does not exclude irregular particular solution $\psi \propto r^{-\ell-1}$ for s states of the Coulomb problem [4] hence it is excluded by hand both in Schrödinger's paper [1] and

in the textbooks. Requirement of self-adjointness does not lead to a unique eigenvalue problem since a theorem [5, 6] of Sturm-Liouville theory of differential equations states that *any* of following two types of boundary conditions are consistent with self-adjointness of the Liouville operator:

1. *periodic* boundary conditions

$$\psi(a) - \psi(b) = 0, \quad (1a)$$

$$\psi'(a) - \psi'(b) = 0, \quad (1b)$$

2. *homogeneous Robin* boundary conditions

$$\alpha_1 \psi'(a) + \beta_1 \psi(a) = 0, \quad (2a)$$

$$\alpha_2 \psi'(b) + \beta_2 \psi(b) = 0, \quad (2b)$$

where α 's and β 's are real constants, a and b denote endpoints of the interval. The theorem can be generalized to partial Sturm-Liouville equations by taking function values and normal derivatives over hypersurfaces of the domain.

Equations (1) are known as Born - von Kármán [7] or Bloch [8] boundary conditions of the solid state physics. In view of above and Bloch's theorem we can state that *eigenfunctions of aperiodic systems satisfy homogeneous Robin boundary conditions*. Homogeneous Dirichlet and Neumann boundary conditions for model problems of textbooks are special cases of Eqs. (2). Boundary conditions (2) can be divided by arbitrary constants so coefficients $\alpha_i/\sqrt{\alpha_i^2 + \beta_i^2} \equiv \sin \gamma_i$ and $\beta_i/\sqrt{\alpha_i^2 + \beta_i^2} \equiv \cos \gamma_i$ define angles γ_1 and γ_2 representing the boundaries. Random coefficients for amorphous materials, in the Wannier [9] representation, may be interpreted as random walk of these "phase points" around the unit circle which leads to a band structure similarly to the periodic boundary conditions.

As an example of Eqs. (2) let us recover hidden boundary conditions for a non-relativistic H -like ion with nuclear charge Z using known properties of hydrogenic

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bound-state wave functions. Normalization condition guarantees a part of boundary conditions, namely, vanishing at infinity [2]. Asymptotic exponential decay of wave function $\psi = \psi(\mathbf{r})$ is described by limit of logarithmic derivative

$$\lim_{r \rightarrow \infty} \frac{1}{\psi} \frac{\partial \psi}{\partial r} = -\sqrt{-2E}, \quad (3)$$

where and throughout this paper atomic units ($\hbar = e = m_e = 4\pi\epsilon_0 = 1$) are used. Normalization condition results in a mild singularity (a hyperconical cusp) of the wave function [2]: whereas it is continuous everywhere, its directional derivatives are bounded but discontinuous at the Coulomb singularity. Since eigenfunctions of the central field problem are separable as $\psi = R_{n\ell}(r)Y_{\ell m}(\vartheta, \varphi)$, their directional logarithmic derivatives are of the form

$$\frac{\mathbf{e} \cdot \nabla \psi}{\psi} = \frac{\mathbf{e} \cdot \mathbf{e}_r}{R_{n\ell}} \frac{dR_{n\ell}}{dr} + \frac{\mathbf{e} \cdot \mathbf{e}_\vartheta}{Y_{\ell m} r} \frac{\partial Y_{\ell m}}{\partial \vartheta} + \frac{\mathbf{e} \cdot \mathbf{e}_\varphi}{Y_{\ell m} r \sin \vartheta} \frac{\partial Y_{\ell m}}{\partial \varphi},$$

where \mathbf{e} stands for unit vector of the selected direction, $\{\mathbf{e}_r, \mathbf{e}_\vartheta, \mathbf{e}_\varphi\}$ is the basis of the spherical polar coordinate system. In radial directions defined by $\mathbf{e} \cdot \mathbf{e}_r = \pm 1$ and $\mathbf{e} \cdot \mathbf{e}_\vartheta = \mathbf{e} \cdot \mathbf{e}_\varphi = 0$, above expression reduces to

$$\frac{\mathbf{e} \cdot \nabla \psi}{\psi} = \frac{\pm 1}{R_{n\ell}} \frac{dR_{n\ell}}{dr} = \frac{\pm 1}{\psi} \frac{\partial \psi}{\partial r}.$$

Since radial wave function $R_{n\ell} = r^\ell u_{n\ell}(r)$ of the central field problem has a root of multiplicity ℓ at the origin the l'Hospital rule should be applied ℓ times in order to obtain a definite limit

$$\lim_{r \rightarrow 0} \frac{1}{R_{n\ell}} \frac{dR_{n\ell}}{dr} = \lim_{r \rightarrow 0} \frac{R_{n\ell}^{(\ell+1)}}{R_{n\ell}^{(\ell)}} = (\ell + 1) \frac{u'_{n\ell}(0)}{u_{n\ell}(0)} = -Z,$$

where differentiation rules (A1a), (A1b) and explicit forms of the hydrogenic wave functions are used. The discontinuity of the radial logarithmic derivative at the nucleus is then characterized by

$$\lim_{\mathbf{r} \rightarrow \pm 0} \frac{1}{\psi} \frac{\partial \psi}{\partial r} = \lim_{\mathbf{r} \rightarrow \pm 0} \frac{\partial_r^{\ell+1} \psi}{\partial_r^\ell \psi} = \mp Z, \quad (4)$$

where

$$\begin{aligned} \mathbf{r} \rightarrow +0 &\equiv (r \rightarrow 0, \vartheta, \varphi), \\ \mathbf{r} \rightarrow -0 &\equiv (r \rightarrow 0, \pi - \vartheta, \pi + \varphi). \end{aligned}$$

Pair of Eqs. (3) and (4) obviously represent homogeneous Robin boundary conditions of the form (2). Similar boundary conditions will be obtained for many-electron wave functions in Sec. III as a result of asymptotic central symmetry of many-electron Hamiltonian both in the vicinity of nuclei and at large distances.

Three decades after historic papers [1] and [2], T. Kato [10] has derived his famous *cusp condition* for many-electron wave functions $\Psi = \Psi(\mathbf{r}|\mathbf{r}_2, \dots, \mathbf{r}_N)$ of which special case for the electron-nucleus coalescence is

$$\left. \frac{\partial \bar{\Psi}}{\partial r} \right|_{r=0} = -Z\Psi(r=0), \quad (5)$$

where Z denotes nuclear charge of atom located at the origin and overline symbol stands for spherical average. Validity of Eq. (5) is limited to the s states, however, it can be generalized to arbitrary values of ℓ similarly to our Eq. (4). Despite the similarity of Eqs. (4) and (5), the latter one cannot be used as an exact boundary condition due to the spherical average. It will be shown in Sec. III that the *spherical average is redundant in Kato's cusp condition* (5) which was already indicated for some specific few-electron systems by Roothaan and Weiss [11] and by Kolos and Roothaan [12].

Since jump of logarithmic derivative at the nucleus is $2Z$ both in one-electron and in many-electron cases, the discontinuity is caused by common terms of the two Hamiltonians, namely, by singular Coulomb potential and by singular kinetic energy of opposite sign as if no other particles were present except the coalescent ones. An electron-electron potential taking part in cancellation of nuclear Coulomb singularity would require a more singular wave function than square-integrable functions hence cusp condition shows an evidence for the normalization condition.

The outline of the paper is as follows. In Sec. II, many-electron wave function will be expanded about singular points in terms of regular and irregular solid spherical harmonics using theory of singular differential equations. It will be shown that three leading terms of expansion about Coulomb singularities exhibit hydrogenic angular dependence. In Sec. III, homogeneous Robin boundary conditions and exact 1st and 2nd order cusp conditions will be derived. In Sec. IV, physical and numerical consequences of our results will be summarized.

Term *asymptotic equality* is used in this paper in the sense of $\lim_{x \rightarrow x_0} [f(x)/g(x)] = 1$. A boldface argument of *ordo* symbol $O(\mathbf{r}^n)$ indicates anisotropy of omitted terms of expansions throughout this paper.

II. BEHAVIOR OF WAVE FUNCTION AT SINGULAR POINTS

Let us consider non-relativistic Hamiltonian describing N particles interacting with each other by Coulomb potentials

$$\hat{H} = -\frac{1}{2} \sum_{i=1}^N \frac{\Delta_i}{m_i} + \sum_{i=1}^{N-1} \sum_{j=i+1}^N \frac{q_i q_j}{r_{ij}}, \quad (6)$$

where m_i and q_i denote mass and charge of the i^{th} particle, respectively ($m_i = 1$ and $q_i = -1$ for electrons and $m_i = 1836A_\nu$, $q_i = Z_\nu$, $\nu = 1, 2, \dots < N$ for nuclei). Electrons and nuclei will be distinguished only in the final results. Spin coordinates are omitted for simplicity. Many-particle wave functions $\Psi = \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ satisfy stationary-state Schrödinger equation

$$\hat{H}\Psi = E\Psi \quad (7)$$

which is singular both at coalescence points $\mathbf{r} = \mathbf{r}_i$ and as $r \rightarrow \infty$. The singularities and other leading terms of the Hamiltonian are isotropic in both limiting cases. In the vicinity of coalescence points, the singular potential contribution of coalescent particles $O(r^{-1})$ and bounded leading term of potential due to remaining non-coalescent particles $O(r^0)$ are isotropic. At infinity, only Coulombic monopole term $O(r^{-1})$ is isotropic, whereas multipole terms $O(\mathbf{r}^{-2})$ are anisotropic.

Particular solutions of a linear ordinary differential equation in the vicinity of an isolated singular point $x_0 = 0$ are of product form $y = f(x)g(x)$, where $f(x)$ ensures correct behavior of y at the singularity [13] and $g(x)$ is a single-valued analytic function (or has at most a logarithmic singularity) which is nonzero at the singular point. For *isotropic singularities* of a partial differential equation, the solution has the form $y = f(r)g(\mathbf{r})$ with $\mathbf{r} \in \mathbb{R}^n$ and $r = \|\mathbf{r}\|$, where $f(r)$ is responsible for correct behavior of y about the singular point and $g(\mathbf{r})$ (reflecting anisotropy [14] of the coefficient functions) is nonzero at the singular point. It will be shown in this section that due to isotropy of singularities of Hamiltonian (6), the wave function about singular points has the following limiting forms

$$\Psi \xrightarrow[\mathbf{r} \rightarrow \mathbf{r}_i]{} r^{\ell_i} u_i(\mathbf{r}), \quad u_i(0) \neq 0, \quad i = 1, 2, \dots, N,$$

$$\Psi \xrightarrow[r \rightarrow \infty]{} e^{\alpha r} r^\beta v(\mathbf{r}), \quad \lim_{r \rightarrow \infty} v(\mathbf{r}) \neq 0, \quad \alpha < 0.$$

In many-body systems, in contrast to the central-field problem, only energy E is conserved throughout the configuration space, square \mathbf{L}^2 and projection L_z of angular momentum are conserved only at singular points

$$[\hat{H}, \hat{\mathbf{L}}^2] \xrightarrow[\mathbf{r} \rightarrow \mathbf{r}_i]{} 0, \quad [\hat{H}, \hat{L}_z] \xrightarrow[\mathbf{r} \rightarrow \mathbf{r}_i]{} 0, \quad (8a)$$

$$[\hat{H}, \hat{\mathbf{L}}^2] \xrightarrow[r \rightarrow \infty]{} 0, \quad [\hat{H}, \hat{L}_z] \xrightarrow[r \rightarrow \infty]{} 0, \quad (8b)$$

where Hamiltonian (6) is rotationally invariant. In the vicinity of singular points quantum numbers ℓ and m have definite values. Eigenfunctions of many-electron Hamiltonian approach eigenfunctions of angular momentum when approaching singular points of Hamiltonian leading to *asymptotic hydrogenic angular dependence* of wave function

$$\Psi \xrightarrow[\mathbf{r} \rightarrow \mathbf{r}_i]{} R_i(r) Y_{\ell_i m_i}(\vartheta, \varphi), \quad (9a)$$

$$\Psi \xrightarrow[r \rightarrow \infty]{} R_\infty(r) Y_{00}, \quad (9b)$$

where power and exponential functions reflecting singularities are included in the radial functions. In other words, molecular symmetries manifest only at molecular distances, where many-body Hamiltonian does not commute with angular momentum.

A. Asymptotic behavior at infinity

Let us consider an electron, say particle 1, separated from the rest of the system ($m_1 = 1$, $q_1 = -1$ and

$r_1 > r_2, \dots, r_N$). Let us introduce reduced mass M' and center of mass \mathbf{R}' of the whole system, center of mass \mathbf{R}'' of particles except the electron located at \mathbf{r}_1 and their separation \mathbf{r} :

$$\frac{1}{M'} \equiv \sum_{i=1}^N \frac{1}{m_i}, \quad \mathbf{R}' \equiv \frac{\sum_{i=1}^N m_i \mathbf{r}_i}{\sum_{i=1}^N m_i}, \quad \mathbf{R}'' \equiv \frac{\sum_{i=2}^N m_i \mathbf{r}_i}{\sum_{i=2}^N m_i},$$

$$\mathbf{r} \equiv \mathbf{r}_1 - \mathbf{R}'' \equiv (r, \vartheta, \varphi) \equiv (r, \omega).$$

Using Laplace expansion for $r > r_i$

$$\frac{1}{|\mathbf{r} - \mathbf{r}_i|} = \sum_{\lambda=0}^{\infty} \sum_{\mu=-\lambda}^{\lambda} \frac{4\pi}{2\lambda+1} \frac{r_i^\lambda}{r^{\lambda+1}} Y_{\lambda\mu}^*(\omega) Y_{\lambda\mu}(\omega_i)$$

the potential energy can be expressed at large distances as

$$U(\mathbf{r}) = \sum_{\lambda, \mu} \frac{4\pi q_1}{2\lambda+1} \frac{Y_{\lambda\mu}^*(\omega)}{r^{\lambda+1}} \sum_{i=2}^N q_i r_i^\lambda Y_{\lambda\mu}(\omega_i)$$

$$= \frac{q_1}{r} \sum_{i=2}^N q_i + O(\mathbf{r}^{-2}) = -\frac{Q+1}{r} + O(\mathbf{r}^{-2}),$$

where $Q \equiv \sum_{i=1}^N q_i$ by noting that $Q = 0$ for neutral systems.

Due to asymptotic isotropy (8b) of Hamiltonian the many-particle Schrödinger equation is asymptotically separable (9b) in terms of spherical polar coordinates as $r \rightarrow \infty$. Asymptotic radial wave function $R = R(r|\mathbf{r}_2, \dots, \mathbf{r}_N)$ satisfies differential equation [15]

$$\left[-\frac{\Delta_r}{2M'} - \frac{Q+1}{r} - E + O(\mathbf{r}^{-2}) \right] R \xrightarrow[r \rightarrow \infty]{} 0, \quad (10)$$

which is not an eigenvalue equation and E is eigenvalue of Eq. (7). The equation has an isolated *essential* singularity at infinity since transformation of variable $z \equiv 1/r$ leads to 2nd order differential equation

$$z^4 R''(z) + 2M' [E + (Q+1)z + O(z^2)] R(z) \xrightarrow[z \rightarrow 0]{} 0$$

with an isolated 4th order pole at the origin. The pole being independent of potential is a consequence of the Laplacian. Radial equation (10) is of Hamburger type [6, 16]

$$\frac{d^2 R}{dr^2} + \left(a_0 + \frac{a_1}{r} + \frac{a_2}{r^2} + \dots \right) \frac{dR}{dr} + \left(b_0 + \frac{b_1}{r} + \frac{b_2}{r^2} + \dots \right) R = 0$$

with

$$a_1 = 2, \quad a_0 = a_2 = a_3 = \dots = 0,$$

$$b_0 = 2M'E, \quad b_1 = 2M'(Q+1),$$

b_2 and higher order coefficients are anisotropic. Due to essential singularity of the equation the solution vanishes

transcendentally as $r \rightarrow \infty$. Seeking the solution in the form

$$R = e^{\alpha r} u(r), \quad \lim_{r \rightarrow \infty} u(r) \neq 0$$

we obtain

$$\frac{d^2 u}{dr^2} + 2 \left(\alpha + \frac{1}{r} \right) \frac{du}{dr} + \left[\alpha^2 + b_0 + \frac{2\alpha + b_1}{r} + O(r^{-2}) \right] u \xrightarrow{r \rightarrow \infty} 0.$$

By equating leading term of coefficient of $u(r)$ to zero we obtain *indicial equation* of which roots are

$$\alpha = \pm \sqrt{-b_0},$$

where only minus sign leads to a bounded solution. Non-essential singularity of the latter differential equation can be removed by substitution

$$u = r^\beta v(r), \quad \lim_{r \rightarrow \infty} v(r) \neq 0$$

yielding

$$\frac{d^2 v}{dr^2} + 2 \left(\alpha + \frac{\beta + 1}{r} \right) \frac{dv}{dr} + \left[\frac{2\alpha(\beta + 1) + b_1}{r} + O(r^{-2}) \right] v \xrightarrow{r \rightarrow \infty} 0.$$

By equating leading term of coefficient of $v(r)$ to zero we obtain indicial equation with only root

$$\beta = -\frac{b_1}{2\alpha} - 1 = \frac{b_1}{2\sqrt{-b_0}} - 1.$$

In case of a central-symmetric problem the solution of latter differential equation would be of the form

$$v = v_0 + v_1 r^{-1} + v_2 r^{-2} + \dots, \quad (v_0 \neq 0)$$

but since b_2 is anisotropic we restrict our solution to v_0 . The radial wave function at large distances is then [17]

$$R \xrightarrow{r \rightarrow \infty} e^{-\sqrt{-2M'E} r} r^{\frac{M'(Q+1)}{\sqrt{-2M'E}} - 1} [v_0 + O(r^{-1})]. \quad (11)$$

Since above function completely characterizes singularity of Hamiltonian at infinity the many-electron wave function can be expanded in terms of irregular solid spherical harmonics as

$$\Psi = e^{-\sqrt{-2M'E} r} r^{\frac{M'(Q+1)}{\sqrt{-2M'E}}} \sum_{\lambda, \mu} \frac{v_{\lambda\mu}(r^{-1})}{r^{\lambda+1}} Y_{\lambda\mu}(\vartheta, \varphi), \quad (12)$$

where $v_0 = \sqrt{4\pi} v_0 = \text{constant}$. Molecular or crystalline symmetries are reflected by relations between coefficient functions $v_{\lambda\mu}(r^{-1}) \equiv v_{\lambda\mu}(r^{-1}|\mathbf{r}_2, \dots, \mathbf{r}_N)$ for $\lambda > 0$.

B. Local behavior at Coulomb singularities

Let us focus now our attention on coalescence of any two particles, say 1 and 2, while keeping remaining particles separated from them ($r_1, r_2 < r_3, \dots, r_N$). It is convenient to introduce reduced mass M , center of mass \mathbf{R} and separation \mathbf{r} of these two particles:

$$M \equiv \frac{m_1 m_2}{m_1 + m_2}, \quad \mathbf{R} \equiv \frac{m_1 \mathbf{r}_1 + m_2 \mathbf{r}_2}{m_1 + m_2}, \\ \mathbf{r} \equiv \mathbf{r}_1 - \mathbf{r}_2 \equiv (r, \vartheta, \varphi) \equiv (r, \omega).$$

Many-body Hamiltonian (6) can be partitioned as

$$\hat{H} = -\frac{\Delta}{2M} + \frac{q_1 q_2}{r} + \hat{W} + \hat{G}, \quad (13)$$

where

$$\hat{W} \equiv \sum_{i=3}^N \left(\frac{q_1}{r_{1i}} + \frac{q_2}{r_{2i}} \right) q_i, \\ \hat{G} \equiv -\frac{\Delta_{\mathbf{R}}}{2(m_1 + m_2)} - \sum_{i=3}^N \frac{\Delta_i}{2m_i} + \sum_{i=3}^{N-1} \sum_{j=i+1}^N \frac{q_i q_j}{r_{ij}}.$$

Use of Laplace expansion for $r < r'$

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} = \sum_{\lambda=0}^{\infty} \sum_{\mu=-\lambda}^{\lambda} \frac{4\pi}{2\lambda+1} \frac{r^\lambda}{r'^{\lambda+1}} Y_{\lambda\mu}^*(\omega) Y_{\lambda\mu}(\omega')$$

yields

$$W = \sum_{\lambda, \mu} \frac{4\pi w_{\lambda\mu}}{2\lambda+1} [q_1 r_1^\lambda Y_{\lambda\mu}^*(\omega_1) + q_2 r_2^\lambda Y_{\lambda\mu}^*(\omega_2)], \\ w_{\lambda\mu} \equiv w_{\lambda\mu}(\mathbf{r}_3, \dots, \mathbf{r}_N) \equiv \sum_{i=3}^N \frac{q_i}{r_i^{\lambda+1}} Y_{\lambda\mu}(\omega_i).$$

Expressing \mathbf{r}_1 and \mathbf{r}_2 with \mathbf{r} and \mathbf{R} , putting origin of the coordinate system to center of mass \mathbf{R} , using inversion property

$$Y_{\lambda\mu}(\pi - \vartheta, \pi + \varphi) = (-1)^\lambda Y_{\lambda\mu}(\vartheta, \varphi)$$

and addition theorem

$$\frac{4\pi}{2\lambda+1} \sum_{\mu=-\lambda}^{\lambda} Y_{\lambda\mu}(\vartheta_i, \varphi_i) Y_{\lambda\mu}^*(\vartheta, \varphi) = P_\lambda(\cos \gamma_i), \\ \cos \gamma_i \equiv \cos \vartheta \cos \vartheta_i + \sin \vartheta \sin \vartheta_i \cos(\varphi - \varphi_i)$$

we obtain

$$W = \sum_{\lambda=0}^{\infty} \left[\frac{q_1}{m_1^\lambda} + (-1)^\lambda \frac{q_2}{m_2^\lambda} \right] (Mr)^\lambda \sum_{i=3}^N \frac{q_i}{r_i^{\lambda+1}} P_\lambda(\cos \gamma_i) \\ = W_0(r_3, \dots, r_N) + W_1(\mathbf{r}/r, \mathbf{r}_3, \dots, \mathbf{r}_N) r + \dots \quad (14)$$

for potential energy contribution of non-coalescent particles. *For identical coalescent particles, all odd powers of radius vanish* due to the inversion symmetry. This

property has a profound consequence in the behavior of electron-electron potentials which will be discussed in Sec. IV. Leading term of above expansion is constant whereas higher order terms reflecting molecular or crystalline structure are anisotropic. Since average of Legendre polynomials with $\lambda > 0$ vanish the spherical average of W equals to leading constant term of its expansion:

$$\overline{W} \xrightarrow{r \rightarrow 0} (q_1 + q_2) \sum_{i=3}^N \frac{q_i}{r_i} \equiv W_0. \quad (15)$$

Since term \hat{W} of Hamiltonian (13) acts on separation \mathbf{r} of particles 1 and 2 and term \hat{G} acts on their center of mass \mathbf{R} the many-particle Schrödinger equation is separable resulting in an effective one-body problem. The wave equation for $\Psi = \Psi(\mathbf{r}|\mathbf{r}_3, \dots, \mathbf{r}_N)$ has the form

$$\left[-\frac{\Delta}{2M} + \frac{q_1 q_2}{r} + W_0 - E + O(\mathbf{r}) \right] \Psi \xrightarrow{r \rightarrow 0} 0$$

in the vicinity of coalescence points, which is simply a homogeneous differential equation, where E is eigenvalue of Eq. (7). Due to local isotropy (8a) of Hamiltonian (13) the equation is locally separable in terms of spherical polar coordinates and the wave function exhibits local hydrogenic angular dependence of the form (9a) about the origin.

The corresponding radial wave equation

$$-\frac{1}{2Mr^2} \left[\frac{d}{dr} \left(r^2 \frac{d}{dr} \right) - \ell(\ell+1) \right] R + \left[\frac{q_1 q_2}{r} + W_0 - E + O(\mathbf{r}) \right] R \xrightarrow{r \rightarrow 0} 0$$

has an *isolated* singular point at $\mathbf{r} = 0$. Frobenius normal form of this equation is

$$r^2 R'' + rP(r)R' + Q(r)R = 0,$$

where

$$P \equiv 2, \\ Q \equiv -\ell(\ell+1) - 2Mq_1q_2r + 2M(W_0 - E)r^2 + O(r^3).$$

The singular point is *removable* since $P(r)$ and $Q(r)$ are single-valued analytic functions. *Fuchs' theorem* [6, 18] states that in the vicinity of removable singularities, the fundamental system of solutions is

$$R_1 = r^{\lambda_1} u(r), \\ R_2 = r^{\lambda_2} [v(r) + \alpha u(r) \ln r],$$

where $\Re \lambda_1 \geq \Re \lambda_2$, $u(r)$, $v(r)$ are single-valued analytic functions, $u(0) \neq 0$, $v(0) \neq 0$ and α is a constant [19]. The theorem distinguishes three cases for existence of logarithmic term depending on difference $\lambda_1 - \lambda_2$. In order to determine exponents λ_1 and λ_2 we seek the solution in the form $r^\lambda u(r)$. The substitution gives *indicial equation*

$$[\lambda(\lambda-1) + 2\lambda - \ell(\ell+1)] u(r) + O(r) \xrightarrow{r \rightarrow 0} 0$$

of which roots are $\lambda_1 = \ell$ and $\lambda_2 = -\ell - 1$. Since difference $\lambda_1 - \lambda_2 = 2\ell + 1$ is a non-zero integer there is no general rule for existence of logarithmic term hence value of α should be determined individually by substituting R_2 into the differential equation leading to

$$\alpha \xrightarrow{r \rightarrow 0} -r \frac{2Mq_1q_2v(r) + 2\ell v'(r) + O(r)}{(2\ell+1)u(r) + O(r)} \xrightarrow{r \rightarrow 0} 0,$$

i.e. the logarithmic term of the second solution vanishes at the origin hence the fundamental solutions are simply $R_1 = r^\ell u(r)$ and $R_2 = r^{-\ell-1} v(r)$. Since R_2 is unbounded at $r = 0$ the physical solution is

$$R \xrightarrow{r \rightarrow 0} r^\ell u(r). \quad (16)$$

Substituting this expression into the radial equation we obtain differential equation

$$u'' + \frac{2\ell+2}{r} u' - 2M \left[\frac{q_1 q_2}{r} + W_0 - E + O(\mathbf{r}) \right] u \xrightarrow{r \rightarrow 0} 0 \quad (17)$$

of which solution should be analytic according to Fuchs' theorem hence it can be expanded in power series

$$u(r) = u(0) + u'(0)r + \frac{u''(0)}{2!} r^2 + \dots, \quad u(0) \neq 0. \quad (18)$$

Inserting it into the differential equation we obtain algebraic equation

$$-2 [Mq_1q_2u(0) - (\ell+1)u'(0)] r^{-1} \\ + [2M(E - W_0)u(0) - 2Mq_1q_2u'(0) + (2\ell+3)u''(0)] r^0 \\ + O(\mathbf{r}) \xrightarrow{r \rightarrow 0} 0$$

which can be satisfied only if

$$a \equiv \frac{u'(0)}{u(0)} = \frac{Mq_1q_2}{\ell+1}, \quad (19a)$$

$$b \equiv \frac{1}{2} \frac{u''(0)}{u(0)} = \frac{(\ell+1)a^2 + M(W_0 - E)}{2\ell+3}, \quad (19b)$$

where *cusp condition* (19a) removes singularity $O(r^{-1})$ of the equation and relation (19b) represents a *constraint on curvature* of the wave function at the origin [20]. We have to note that $b = b(r_3, \dots, r_N)$ depends on configuration of the non-coalescent particles.

Since singularity of many-particle Hamiltonian (13) is isotropic at $r = 0$ its eigenfunctions have the form

$$\Psi = r^\ell u(\mathbf{r}|\mathbf{r}_3, \dots, \mathbf{r}_N) = r^\ell \sum_{\lambda, \mu} r^\lambda u_{\lambda\mu}(r) Y_{\lambda\mu}(\vartheta, \varphi)$$

in the vicinity of coalescence points which can be considered as the spatial generalization of Frobenius series, where $u_{\lambda\mu}(r) \equiv u_{\lambda\mu}(r|\mathbf{r}_3, \dots, \mathbf{r}_N)$. In view of local commutativity (8a) of angular momentum with Hamiltonian both ℓ and m have definite values at the origin. Since many-particle wave function is antisymmetric under interchange of any two electrons, ℓ takes only even values

for singlet spin states $S = 0$ and odd values for triplet spin states $S = 1$ of coalescent electrons. Since leading terms $\ell(\ell + 1)/2Mr^2$, q_1q_2/r and W_0 of Hamiltonian are isotropic, three leading terms of wave function exhibit hydrogenic angular dependence [21]

$$\Psi \xrightarrow{r \rightarrow 0} r^\ell u_\ell(0) (1 + ar + br^2) Y_{\ell m}(\vartheta, \varphi) + \dots$$

Therefore the many-electron wave function in the vicinity of Coulomb singularities is of the form

$$\Psi = r^\ell u_\ell(r|\mathbf{r}_3, \dots, \mathbf{r}_N) Y_{\ell m}(\vartheta, \varphi) + r^{\ell+3} v(\mathbf{r}|\mathbf{r}_3, \dots, \mathbf{r}_N), \quad (20)$$

where

$$u_\ell = u_\ell(0) (1 + ar + br^2 + cr^3 + \dots),$$

$$v = \sum_{\lambda=\ell+1}^{\infty} \sum_{\mu=-\lambda}^{\lambda} r^{\lambda-\ell-1} v_{\lambda\mu}(r|\mathbf{r}_3, \dots, \mathbf{r}_N) Y_{\lambda\mu}(\vartheta, \varphi).$$

Term $O(r^\ell)$ of expression (20) is an eigenfunction of the spherically averaged Hamiltonian, term $O(r^{\ell+3})$ reflects anisotropy of molecular or crystalline potential [22] [23].

In view of Eq. (15) the limiting form of spherically averaged Hamiltonian is equivalent to that of a Coulomb potential embedded in a uniform background

$$\widehat{H} \xrightarrow{r \rightarrow 0} -\frac{\Delta}{2M} + \frac{q_1q_2}{r} + W_0 \quad (21)$$

hence Eq. (17) can be rewritten as

$$ru'' + (2\ell + 2)u' - (2\alpha + \beta^2r)u = 0,$$

where $\alpha \equiv Mq_1q_2$ and $\beta^2 \equiv 2M(W_0 - E)$. Seeking the solution in the form $u = e^{-\beta r}w(r)$ and then by making change of variable $x \equiv 2\beta r$ we obtain following confluent hypergeometric equation

$$xw'' + (2\ell + 2 - x)w' - (\ell + 1 + \alpha/\beta)w = 0$$

which is of Kummer type [24]

$$xw'' + (\mathbf{b} - x)w' - \mathbf{a}w = 0$$

with $\mathbf{a} = \ell + 1 + \alpha/\beta$ and $\mathbf{b} = 2\ell + 2$. Regular solution of this equation is the following Kummer function [25]

$$w = {}_1F_1(\mathbf{a}; \mathbf{b}; x) \equiv \sum_{k=0}^{\infty} \frac{(\mathbf{a})_k}{(\mathbf{b})_k} \frac{x^k}{k!},$$

where $(\mathbf{a})_k$ denotes the Pochhammer symbol defined by $(\mathbf{a})_k \equiv \Gamma(\mathbf{a} + k)/\Gamma(\mathbf{a})$. Therefore radial wave function of the spherically averaged Hamiltonian is

$$R_\ell \xrightarrow{r \rightarrow 0} r^\ell u_\ell(0) e^{-\beta r} {}_1F_1(\ell + 1 + \alpha/\beta; 2\ell + 2; 2\beta r) \quad (22)$$

in the vicinity of Coulomb singularities (for comparison with an accurate Hartree-Fock-Roothaan atomic wave function see Figs. 1 and 2, for a recurrence relation see

Appendix B). This analytic function fully characterizes cusps of spherically symmetric or spherically averaged systems since arbitrarily high order cusp relations can be derived from it [26]. For anisotropic systems, only 1st and 2nd order cusp conditions (19) are exact which can also be obtained from Taylor coefficients of Eq. (22). This bound-state local solution becomes unphysical at larger distances satisfying $q_1q_2/r + W_0 \geq 0$, where charge of particles within sphere of radius r should also be included. Function (22) is not square-integrable but knowledge of its higher order derivatives at $r = 0$ is useful in numerical calculation of $u_\ell(r)$ used in expansion (20).

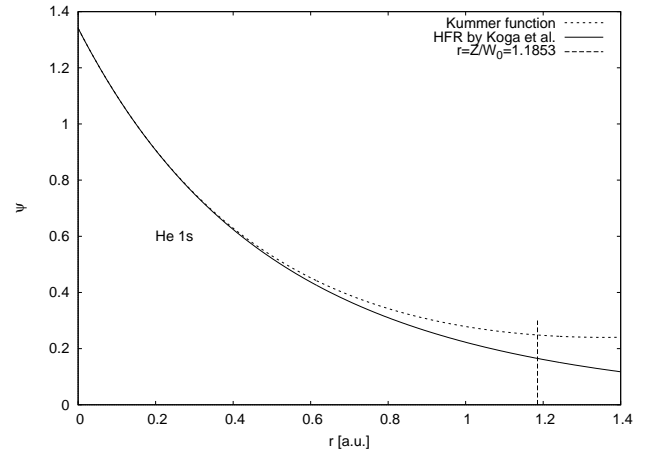


FIG. 1. Wave function of Kummer type (22) compared with Hartree-Fock-Roothaan wave function computed by Koga, Kanayama, Watanabe and Thakkar [27] for ground state of the *He* atom. Radius $r = Z/W_0$ of bound-state region of spherically averaged Hamiltonian (21) is marked on the r axis.

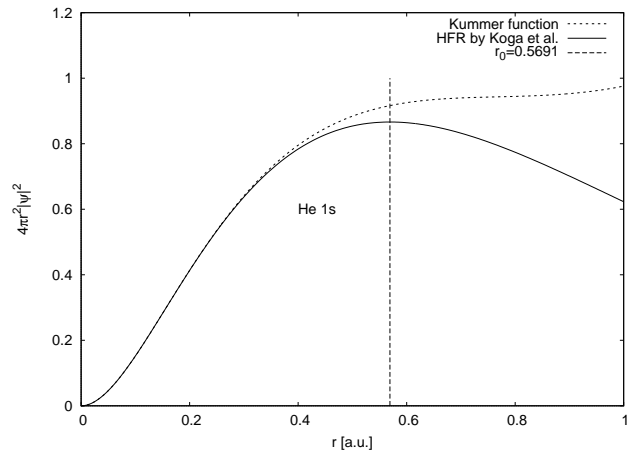


FIG. 2. Radial density obtained from Eq. (22) compared with that of computed by Koga et al. [27] for ground state of the *He* atom. Our near-nucleus approximation is accurate up to surprisingly large distances. Effective Bohr radius r_0 of the orbital is marked on the r axis.

III. CUSP AND BOUNDARY CONDITIONS

Using expansions (12) and (20) of many-electron wave function about singular points of Hamiltonian (6) we are able to recover explicit forms of boundary conditions for the many-electron Schrödinger equation. Due to local isotropy (8) of Hamiltonian at singular points we can follow the same procedure as we did in Sec. I for the H atom. One of our resulted boundary conditions may be considered as an *exact* cusp condition without spherical average which contradicts Kato's result. Using our Kummer function solution (22) for the spherically averaged Hamiltonian we can define arbitrarily high order cusp conditions in the framework of central field approximation.

A. Boundary conditions

In view of expansion (12) of many-electron wave function at large distances, its logarithmic derivative with respect to r is

$$\frac{1}{\Psi} \frac{\partial \Psi}{\partial r} \xrightarrow{r \rightarrow \infty} -\sqrt{-2M'E} + \left[\frac{M'(Q+1)}{\sqrt{-2M'E}} - 1 \right] \frac{1}{r} + O(r^{-2})$$

which defines our first boundary condition:

$$\lim_{r \rightarrow \infty} \frac{1}{\Psi} \frac{\partial \Psi}{\partial r} = -\sqrt{-2M'E}. \quad (23)$$

The directional logarithmic derivative of many-electron wave function in arbitrary direction \mathbf{e} can be expressed in terms of spherical polar coordinates as

$$\frac{\mathbf{e} \cdot \nabla \Psi}{\Psi} = \frac{\mathbf{e} \cdot \mathbf{e}_r}{\Psi} \frac{\partial \Psi}{\partial r} + \frac{\mathbf{e} \cdot \mathbf{e}_\vartheta}{\Psi r} \frac{\partial \Psi}{\partial \vartheta} + \frac{\mathbf{e} \cdot \mathbf{e}_\varphi}{\Psi r \sin \vartheta} \frac{\partial \Psi}{\partial \varphi},$$

where $\{\mathbf{e}_r, \mathbf{e}_\vartheta, \mathbf{e}_\varphi\}$ is the basis of spherical polar coordinate system. In radial directions, defined by $\mathbf{e} \cdot \mathbf{e}_r = \pm 1$ and $\mathbf{e} \cdot \mathbf{e}_\vartheta = \mathbf{e} \cdot \mathbf{e}_\varphi = 0$, above expression reduces to

$$\frac{\mathbf{e} \cdot \nabla \Psi}{\Psi} = \frac{\mathbf{e} \cdot \nabla_r \Psi}{\Psi} = \frac{\pm 1}{\Psi} \frac{\partial \Psi}{\partial r}.$$

Since many-electron wave function $\Psi = r^\ell u(\mathbf{r})$ has a root of multiplicity ℓ at Coulomb singularities the l'Hospital rule should be applied ℓ times in order to obtain a definite limit

$$\frac{1}{\Psi} \frac{\partial \Psi}{\partial r} \xrightarrow{r \rightarrow 0} \frac{\partial_r^{\ell+1} \Psi}{\partial_r^\ell \Psi} \xrightarrow{r \rightarrow 0} \frac{\ell+1}{u(\mathbf{r})} \frac{\partial u(\mathbf{r})}{\partial r} + O(r),$$

where differentiation rules (A2a) and (A2b) are used [28]. Since expansion (20) exhibits hydrogenic angular dependence $r^\ell u_\ell(r) Y_{\ell m}(\vartheta, \varphi)$ in the vicinity of Coulomb singularities the radial logarithmic derivatives of Ψ have the following one-sided limits:

$$\lim_{r \rightarrow \pm 0} \frac{1}{\Psi} \frac{\partial \Psi}{\partial r} = \lim_{r \rightarrow \pm 0} \frac{\partial_r^{\ell+1} \Psi}{\partial_r^\ell \Psi} = \pm (\ell+1) a, \quad (24)$$

where a is defined by Eq. (19a) and

$$\begin{aligned} \mathbf{r} \rightarrow +0 &\equiv (r \rightarrow 0, \vartheta, \varphi), \\ \mathbf{r} \rightarrow -0 &\equiv (r \rightarrow 0, \pi - \vartheta, \pi + \varphi). \end{aligned}$$

Equation (24) is our second boundary condition.

Equations (23) and (24) represent homogeneous Robin boundary conditions for the many-electron wave function and have the same form as Eqs. (3) and (4) obtained for the H atom which is a consequence of asymptotic isotropy (8) of Hamiltonian at singular points.

B. Cusp conditions

Boundary condition (24) is the exact form of first order cusp condition which does not contain spherical average. By substituting specific values of M , q_1 and q_2 into Eq. (24) we obtain cusp conditions for the electron-nucleus coalescence

$$\lim_{r \rightarrow \pm 0} \frac{\partial_r^{\ell+1} \Psi}{\partial_r^\ell \Psi} = \mp \frac{A_\nu}{A_\nu + 1} Z_\nu, \quad \ell = 0, 1, 2, \dots, \quad (25)$$

where A_ν and Z_ν stand for mass and charge of the ν^{th} nucleus, respectively. Similarly we obtain following cusp conditions for electron-electron coalescences

$$\lim_{r \rightarrow \pm 0} \frac{\partial_r^{\ell+1} \Psi_{\uparrow\downarrow}}{\partial_r^\ell \Psi_{\uparrow\downarrow}} = \pm \frac{1}{2}, \quad \ell = 0, 2, 4, \dots, \quad (26a)$$

$$\lim_{r \rightarrow \pm 0} \frac{\partial_r^{\ell+1} \Psi_{\uparrow\uparrow}}{\partial_r^\ell \Psi_{\uparrow\uparrow}} = \pm \frac{1}{2}, \quad \ell = 1, 3, 5, \dots, \quad (26b)$$

where $\uparrow\downarrow$ and $\uparrow\uparrow$ denote singlet and triplet spin states, respectively.

Since 2^{nd} order radial partial derivative $(\mathbf{e} \cdot \nabla_r)^2$ is of definite sign the 2^{nd} order cusp condition has the form

$$\lim_{r \rightarrow 0} \frac{1}{\Psi} \frac{\partial^2 \Psi}{\partial r^2} = \lim_{r \rightarrow 0} \frac{\partial_r^{\ell+2} \Psi}{\partial_r^\ell \Psi} = (\ell+1)(\ell+2)b, \quad (27)$$

where differentiation rules (A2a) and (A2c) are used, b is defined by Eq. (19b).

Coefficient a in Eqs. (24, 27) depends only on charges and masses of the coalescent particles. In view of Eqs. (15) and (19b), coefficient $b = b(r_3, \dots, r_N)$ in Eq. (27) depends on distances of non-coalescent particles hence it should be averaged over all possible configurations and has the same value for the spherically averaged system. Arbitrarily high order cusp conditions can be obtained from Eq. (22) by means of recurrence relation (B1) in the framework of central field approximation. Third and higher order cusp conditions for exact wave functions require spherical average similarly to Kato's cusp condition (5) since higher order coefficients of expansion (20) depend both on distances and directions of the non-coalescent particles.

In view of Eq. (20) the electron pair density exhibits short-range hydrogenic angular dependence in the vicinity of coalescence points hence satisfies exact 1^{st} and 2^{nd} order cusp conditions similar to Eqs. (26) and (27).

IV. CONSEQUENCES

A. Physical Consequences

Potential energy term W_0 defined by Eq. (15) is related to the NMR chemical shift since it is proportional to ratio $H_i(0)/H$ of induced diamagnetic shielding field to the applied external magnetic field [29, 30].

We saw that all odd powers vanish in expansion (14) of potential $W(\mathbf{r})$ about electron-electron coalescences ($q_1 = q_2$ and $m_1 = m_2$) due to their inversion symmetry in the center of mass system. Hence electron-electron potentials are even functions of interparticle separation in the vicinity of coalescence points regardless of molecular or crystalline symmetry. A nearly quadratic behavior of exchange-correlation potential was observed by Umrigar and Gonze [31] without explanation, saying "we know of no theoretical reason why this must be rigorously true". Nagy and Sen [32] obtained exact quadratic behavior of spherically averaged Kohn-Sham potential around the nuclei in the framework of heavy nucleus approximation. Qian and Sahní [33] found a small linear term "which is solely due to correlation-kinetic effects". From author's point of view these effects are specific to the density functional theory (DFT).

Expansion (20) characterizes short-range behavior of many-electron wave function both in the vicinity of electron-nucleus and electron-electron coalescences hence can be used to describe short-range electron correlation, where parameter $b = (r_3, \dots, r_N)$ represents the chemical environment. First order cusp condition (19a, 24) is responsible for boundedness of many-electron wave function at Coulomb singularities by exactly canceling singular kinetic and potential energy terms. Second order cusp condition (19b, 27) enforces correct value E of local energy $E_{loc} \equiv \Psi^{-1} \hat{H} \Psi$ at Coulomb singularities by imposing constraints on curvature of many-electron wave function. These conditions are exact for arbitrary values of ℓ and do not need spherical average in contrast to Kato's cusp condition (5). It follows from Eq. (22) that all radial partial derivatives of eigenfunctions of spherically averaged Hamiltonian at coalescence points depend on the same constant quantities: ℓ , q_1 , q_2 , M , E and W_0 . Third and higher order derivatives of exact eigenfunctions depend on anisotropic multipole potential terms of expansion (14) as well. In view of Eq. (20), symmetry considerations apply only to terms $O(\mathbf{r}^{\ell+3})$ and of higher orders.

B. Numerical consequences

If both boundary conditions are known the numerical solution of Schrödinger equation over a grid yields an algebraic eigenvalue problem which can be solved by means of Jacobi - Goldstine - Murray - von Neumann diagonalization algorithm [34]. Before Kato's cusp condi-

tion only long-range behavior (23) of wave function was known hence a numerical trick called *shooting method* was used to substitute the missing boundary condition at Coulomb singularities. This method is best suited to equidistant grids, where inward and outward numerical integrations are equally accurate. Since most of energy is concentrated at near-nucleus regions the practical grids used in quantum chemistry are substantially finer in the vicinity of nuclei than in the interstitial and exterior regions. The grid is coarsest at large distances representing ∞ in the numerical calculation hence an outward integrated solution starting from a guessed initial condition is fitted at a midpoint to an inward integrated solution based on an inaccurate initial condition. Kato's cusp condition (5) is suitable only to the central-field approximation and cannot be used as an exact boundary condition. Our boundary conditions (23) and (24) are exact regardless of molecular or crystalline symmetry since the wave function exhibits hydrogenic angular dependence in both limiting cases. A shooting method based on our cusp condition (24) would be more accurate than the traditional one due to the finer grid at nuclei. Since both boundary conditions are known one can transform Schrödinger equation to an algebraic eigenvalue problem instead of performing the time-consuming shooting loop. Approximate wave function (22) can be used to find optimal near-nucleus step size for the grid.

Basis sets satisfying cusp conditions improve convergence of Hartree-Fock-Roothaan variational calculations. It is well known that Slater-type basis sets satisfy 1st order cusp condition if exponential decay parameter of one basis function is appropriately fixed

$$R(r) = c_0 r^\ell e^{-\frac{Zr}{\ell+1}} + \sum_{\lambda=1}^L c_\lambda r^{\ell+\lambda} e^{-\zeta_\lambda r}$$

letting only its weight factor c_0 to be varied. Similar basis set was used by Roothaan and Kelly [35] however their summation inexplicably starts from $\lambda = 3$ resulting in slow convergence for $\ell > 0$ hence use of cusp condition was limited to the s orbitals in their atomic calculations. It is easy to construct a Slater-type basis set satisfying both 1st and 2nd order cusp conditions by equating three leading expansion coefficients of linear combination of two Slater functions with equal exponential factors to that of expansion (18) yielding

$$R = c_0 r^\ell \left[1 + \left(b - \frac{a^2}{2} \right) r^2 \right] e^{ar} + \sum_{\lambda=3}^L c_\lambda r^{\ell+\lambda} e^{-\zeta_\lambda r},$$

where a and b are defined by Eqs. (19). In order to preserve asymptotic behavior of wave function as $r \rightarrow \infty$ a Slater function of the form (11) should be added to the basis set.

It is widely believed that Gaussian basis sets are not suitable to describe nuclear cusps since they have zero gradients at the nuclei which is true only for individual Gauss functions but not for their linear combinations.

By equating three leading expansion coefficients of linear combination of three Gauss functions with equal exponential factors to that of expansion (18) we obtain Gaussian basis set

$$\psi(x, y, z) = c_0 r^\ell [1 + ar + (b + g_0) r^2] e^{-g_0 r^2} Y_{\ell m}(\vartheta, \varphi) + \sum_{i+j+k \geq \ell+3}^L c_{ijk} x^i y^j z^k e^{-g_{ijk} r^2}$$

satisfying both 1st and 2nd order cusp conditions, where a and b are defined by Eqs. (19) and $r^2 = x^2 + y^2 + z^2$. There is no finite linear combination of Gauss functions which exhibits asymptotic behavior (11) of wave function as $r \rightarrow \infty$. Use of basis functions satisfying both 1st and 2nd order electron-electron cusp conditions provides the simplest way to include short-range correlation effects.

Asymptotic hydrogenic angular dependence of three leading terms of expansion (20) of many-electron wave function about Coulomb singularities explains the success of central-field approximation in atomic calculations and muffin-tin approximation in the solid state physics. Kummer-type confluent hypergeometric function (22) intended to characterize the short-range behavior of eigenfunctions $r^\ell u_\ell(r) Y_{\ell m}(\vartheta, \varphi)$ of the spherically averaged Hamiltonian is surprisingly accurate even at relatively large distances, e.g. one can see from Fig. 2 that relative error of this approximation to radial density $4\pi r^2 |\psi|^2$ is 5.8% at the effective Bohr radius and is 0.4% at its half. Therefore the spherically averaged part of Hamiltonian is responsible for most of the effects and anisotropic terms can be considered as perturbations.

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Appendix A: Some differentiation rules

Leibniz's theorem for differentiation of products states

$$[f(x)g(x)]^{(n)} = \sum_{k=0}^n \binom{n}{k} f^{(n-k)}(x) g^{(k)}(x).$$

For $f(x) = x^\ell$ we obtain

$$[x^\ell g(x)]^{(n)} = \sum_{k=0}^n \binom{n}{k} \frac{\ell! x^{\ell-n+k} g^{(k)}(x)}{(\ell-n+k)!}.$$

Specific higher order derivatives of the above type used in this paper are

$$[x^\ell g(x)]^{(\ell)} \xrightarrow{x \rightarrow 0} \ell! g(0) + O(x), \quad (\text{A1a})$$

$$[x^\ell g(x)]^{(\ell+1)} \xrightarrow{x \rightarrow 0} (\ell+1)! g'(0) + O(x), \quad (\text{A1b})$$

$$[x^\ell g(x)]^{(\ell+2)} \xrightarrow{x \rightarrow 0} (\ell+2)! g''(0) + O(x). \quad (\text{A1c})$$

For higher order radial partial derivatives of $r^\ell u(\mathbf{r})$ we obtain similarly

$$\frac{\partial^\ell r^\ell u(\mathbf{r})}{\partial r^\ell} \xrightarrow{r \rightarrow 0} \ell! u(0) + O(\mathbf{r}), \quad (\text{A2a})$$

$$\frac{\partial^{\ell+1} r^\ell u(\mathbf{r})}{\partial r^{\ell+1}} \xrightarrow{r \rightarrow 0} (\ell+1)! \left. \frac{\partial u}{\partial r} \right|_{r=0} + O(\mathbf{r}), \quad (\text{A2b})$$

$$\frac{\partial^{\ell+2} r^\ell u(\mathbf{r})}{\partial r^{\ell+2}} \xrightarrow{r \rightarrow 0} (\ell+2)! \left. \frac{\partial^2 u}{\partial r^2} \right|_{r=0} + O(\mathbf{r}). \quad (\text{A2c})$$

Quotients of above derivatives become isotropic if $u(\mathbf{r})$ can be written as a product of radial and angular parts.

Appendix B: Series expansion of function (22)

Solution of Eq. (17) in the vicinity of $r = 0$ is

$$u_\ell(r) = e^{-\beta r} {}_1F_1(\ell+1 + \alpha/\beta; 2\ell+2; 2\beta r)$$

with $\alpha \equiv Mq_1q_2$ and $\beta^2 \equiv 2M(W_0 - E)$. By substituting power series $u_\ell(r) = \sum_{k=0}^{\infty} a_k r^k$ into the equation we obtain following boundary condition and three-term recurrence relation

$$a_1 = \frac{\alpha}{\ell+1} a_0, \quad (\text{B1a})$$

$$a_{k+1} = \frac{2\alpha a_k + \beta^2 a_{k-1}}{(2\ell+2+k)(k+1)} \quad k = 1, 2, \dots, \quad (\text{B1b})$$

providing a simple way of generating higher order cusp conditions for eigenfunctions of spherically averaged Hamiltonian (21).

[1] E. Schrödinger, *Ann. Phys.* **79**, 361 (1926).

[2] J. von Neumann, *Gött. Nachr., Math.-Phys.*, 1(1927), <http://gdz.sub.uni-goettingen.de/>.

[3] Cf. Eqs. (6) and (24) of Ref. [1].

[4] L. E. Ballentine, *Quantum Mechanics* (World Scientific, Singapore, 1998) Sec. 4.5.

[5] G. A. Korn and T. M. Korn, *Mathematical Handbook for Scientists and Engineers*, 2nd ed. (McGraw-Hill, New York, 1968) Sec. 15.4.8.

[6] E. L. Ince, *Ordinary Differential Equations* (Dover, New York, 1944).

[7] M. Born and T. von Kármán, *Phys. Z.* **13**, 297 (1912); **14**, 15 (1913); **14**, 65 (1913).

[8] F. Bloch, *Z. Phys.* **52**, 555 (1928).

[9] G. H. Wannier, *Phys. Rev.* **52**, 191 (1937).

[10] T. Kato, *Commun. Pure Appl. Math.* **10**, 151 (1957).

[11] C. C. J. Roothaan and A. W. Weiss, *Rev. Mod. Phys.* **32**, 194 (1960).

- [12] W. Kolos and C. C. J. Roothaan, *Rev. Mod. Phys.* **32**, 205 (1960).
- [13] It is typically power, exponential or Gaussian function.
- [14] One may expand it in 3 dimensions in terms of regular $r^\lambda Y_{\lambda\mu}(\vartheta, \varphi)$ or irregular $r^{-\lambda-1} Y_{\lambda\mu}(\vartheta, \varphi)$ solid spherical harmonics.
- [15] Centrifugal kinetic energy term is omitted since it has the same order as omitted anisotropic dipole term of the potential energy.
- [16] V. I. Smirnov, *Kurs vysshey matematiki*, 9th ed., Vol. III/2 (Nauka, Moskva, 1974) Sec. V.16; English translation: *A Course of Higher Mathematics*, Vol. 3 (Pergamon Press, Oxford, 1964).
- [17] This behavior is in accordance with results of J. Katriel and E. R. Davidson, *Proc. Natl. Acad. Sci. USA* **77**, 4403 (1980).
- [18] L. Schlesinger, *Einführung in die Theorie der Differentialgleichungen*, Sammlung Schubert No. XIII (Götschen, Leipzig, 1900) Chap. 3, quoted by Schrödinger [1]; E. T. Whittaker and G. N. Watson, *A Course of Modern Analysis*, 4th ed. (Cambridge University Press, 1963) Chap. X.
- [19] Transformation of r to a dimensionless variable required by the logarithmic term is omitted for brevity.
- [20] Leading expansion coefficients of radial wave functions of the H atom are the same as Eqs. (19) with $W_0 = 0$.
- [21] An anisotropic linear term $\mathbf{e} \cdot \mathbf{r}$ was introduced in a mathematically questionable way by W. A. Bingel, *Z. Naturforsch.* **18a**, 1249 (1963); recently generalized by X.-Y. Pan and V. Sahni, *J. Chem. Phys.* **119**, 7083 (2003).
- [22] According to Fuchs' theorem $u_\ell(0) \neq 0$ but $v_{\lambda\mu}(0)$ may vanish since they are not related to the singularity. Cusp condition of the form (19a) was obtained for *all* partial waves by R. T. Pack and W. B. Brown, *J. Chem. Phys.* **45**, 556 (1966) as a result of careless use of calculus.
- [23] Due to local conservation of angular momentum (8a) the summation over m is redundant in similar expansions found in the literature, e.g. in Ref. [32].
- [24] *Handbook of Mathematical Functions*, edited by M. Abramowitz and I. A. Stegun (National Bureau of Standards, Washington, D.C., 1972) <http://dlmf.nist.gov/13>.
- [25] The solution reduces to associated Laguerre polynomial in case of $W_0 = 0$. We may formally consider $-\alpha/\beta$ as a non-integer principal quantum number.
- [26] Higher order cusp conditions obtained from Kummer type wave function (22) agree with that of Refs. [36] and [32] (after typographic correction $Z_\alpha \mapsto Z_\alpha^2$).
- [27] T. Koga, K. Kanayama, S. Watanabe, and A. J. Thakkar, *Int. J. Quantum Chem.* **71**, 491 (1999).
- [28] In general, radial partial derivative of an anisotropic function is anisotropic which explains appearance of spherical average in Kato's cusp condition (5). See discussion after the statement of Theorem IIa in Ref. [10].
- [29] W. E. Lamb, *Phys. Rev.* **60**, 817 (1941).
- [30] W. C. Dickinson, *Phys. Rev.* **80**, 563 (1950).
- [31] C. J. Umrigar and X. Gonze, *Phys. Rev. A* **50**, 3827 (1994).
- [32] Á. Nagy and K. D. Sen, *J. Chem. Phys.* **115**, 6300 (2001).
- [33] Z. Qian and V. Sahni, *Phys. Rev. A* **75**, 032517 (2007).
- [34] H. H. Goldstine, F. J. Murray, and J. von Neumann, *J. ACM* **6**, 59 (1959).
- [35] C. C. J. Roothaan and P. S. Kelly, *Phys. Rev.* **131**, 1177 (1963). We suppose that summation starting from $\lambda = 3$ arises from some unpublished expansion similar to our Eq. (20), where $u_\ell(r)$ was simply replaced by $e^{-Zr/(\ell+1)}$.
- [36] V. A. Rassolov and D. M. Chipman, *J. Chem. Phys.* **104**, 9908 (1996).