Criticality of Electron-Nucleus Cusp Condition to Local Effective Potential Energy Theories

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Abstract

Local(multiplicative) effective potential energy theories of electronic structure comprise the transformation of the Schrödinger equation for interacting fermi systems to model noninteracting fermi or bose systems whereby the equivalent density and energy are obtained. By employing the integrated form of the Kato electron-nucleus cusp condition, we prove that the effective electron-interaction potential energy of these model fermions or bosons is finite at a nucleus. The proof is general and valid for arbitrary system whether it be atomic, molecular, or solid state, and for arbitrary state and symmetry. This then provides justification for all prior work in the literature based on the assumption of finiteness of this potential energy at a nucleus. We further demonstrate the criticality of the electron-nucleus cusp condition to such theories by example of the Hydrogen molecule. We show thereby that both model system effective electron-interaction potential energies, as determined from densities derived from accurate wave functions, will be singular at the nucleus unless the wave function satisfies the electron-nucleus cusp condition.
I. INTRODUCTION

Consider the time-independent Schrödinger equation for atoms, molecules, or solids:

\[ \hat{H} \Psi(r_1, \ldots, r_N) = E \Psi(r_1, \ldots, r_N), \tag{1} \]

where \( \Psi(r_1, \ldots, r_N) \) is the system wave function, \( E \) the energy, and \( N \) the number of electrons. (We suppress the spin coordinate throughout the paper.) The electronic Hamiltonian \( \hat{H} \) in atomic units is

\[ \hat{H} = -\frac{1}{2} \sum_i \nabla_i^2 + \sum_i v(r_i) + \frac{1}{2} \sum_{i,j} \frac{1}{|r_i - r_j|}, \tag{2} \]

where the first and last terms represent the electron kinetic and electron interaction potential energy operators, respectively, and \( v(r) \) the operator representing the potential energy of the electrons due to the external charge \( Z \) of the nuclei at \( R_\alpha \): \( v(r) = \sum_\alpha \frac{Z}{|r - R_\alpha|}. \tag{3} \)

The electronic density \( \rho(r) \) of the system is defined as

\[ \rho(r) = N \int \psi^*(r, r_2, \ldots, r_N) \psi(r, r_2, \ldots, r_N) \, dr_2 \ldots dr_N. \tag{4} \]

At the coalescence of an electron with a nucleus, the external potential energy operator \( v(r) \) is singular. For the wave function to satisfy the Schrödinger equation and remain bounded, it must satisfy the Kato [1] electron nucleus cusp condition at each nucleus. The cusp condition is usually stated in differential form [1]. In integrated form, the statement of the cusp condition for arbitrary state of the system is [2, 3]

\[ \psi(r, r_2, \ldots, r_N) = \psi(0, r_2, \ldots, r_N). (1 - Zr) + r \cdot a(r_2, \ldots, r_N) + O(r^2), \tag{5} \]

where the vectors \( r_i \) now represent the positions of the electrons from a particular nucleus. The vector \( a(r_2, \ldots, r_N) \) is undetermined. The derivation of the integrated form of the cusp condition does not involve any boundary conditions far from the nucleus. Hence, it is valid at the nuclei of atoms, molecules, and periodic and aperiodic solids.

In addition to solving the Schrödinger equation (1), electronic structure is also determined by calculations performed within the framework of local(multiplicative) effective potential energy theories. Representative of such theories are Kohn-Sham density functional theory
(KS-DFT) [4], the Optimized Potential Method (OPM) [5], and quantal density functional theory (Q-DFT) [6]. The basic idea underlying such theories is the transformation of the Schrödinger equation to that of the model S system of noninteracting fermions whereby the equivalent density $\rho(\mathbf{r})$ and energy $E$ are obtained. The differential equation describing the model fermions is

$$\left[ -\frac{1}{2} \nabla^2 + v_s(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}); \ i = 1, 2, \ldots, N, \quad (6)$$

where $v_s(\mathbf{r})$ is their effective potential energy:

$$v_s(\mathbf{r}) = v(\mathbf{r}) + v_{ee}(\mathbf{r}), \quad (7)$$

with $v_{ee}(\mathbf{r})$ their effective electron-interaction potential energy. The potential energy $v_{ee}(\mathbf{r})$ accounts for electron correlations due to the Pauli exclusion principle and Coulomb repulsion, and Correlation-Kinetic effects which are a consequence of the difference in the kinetic energy of the interacting and noninteracting systems. The various theories differ in their definitions of the potential energy $v_{ee}(\mathbf{r})$. In KS-DFT, the energy $E$ is a functional of the ground state density $\rho(\mathbf{r})$, and $v_{ee}(\mathbf{r})$ is defined as the functional derivative of its KS electron-interaction energy $E_{KS}^{ee}[\rho]$ component. In the OPM, this energy component is considered a functional of the orbitals $\phi_i(\mathbf{r}) : E_{ee}^{KS} = E_{ee}^{KS}[\phi_i]$. The potential energy $v_{ee}(\mathbf{r})$, defined as the functional derivative of $E_{ee}^{KS}[\phi_i]$, is obtained by solution of an integral equation in conjunction with the differential equation (6). Within Q-DFT, the potential energy $v_{ee}(\mathbf{r})$ is the work done to move the model fermion in a conservative field $\mathcal{F}_s(\mathbf{r})$. The density $\rho(\mathbf{r})$ equivalent to that of the interacting system Eq. (4) is determined from the orbitals $\phi_i(\mathbf{r})$ as

$$\rho(\mathbf{r}) = \sum_i |\phi_i(\mathbf{r})|^2. \quad (8)$$

The energy is determined from the energy functionals, or in terms of the components of the conservative field. The highest occupied eigenvalue of the differential equation is the negative of the ionization energy [7, 8, 9].

An understanding of the structure and general properties of the potential energy $v_{ee}(\mathbf{r})$ that allows for the transformation from the interacting to the noninteracting model system is therefore of importance. The structure is also of significance for the evaluation and construction of approximations within the various S system theories. A key aspect of this structure, and one that has been controversial, is whether the potential energy $v_{ee}(\mathbf{r})$ is
finite or singular at a nucleus. The principal manner by which the structure is determined
is one that employs methods which assume knowledge of the exact density $\rho(r)$. The
densities in turn are obtained from correlated or configuration-interaction wave functions
that are highly accurate from the total energy perspective. Work on the He atom by Smith
et al, Davidson, and Umrigar and Gonze, show $v_{ee}(r)$ to be finite at the
nucleus. Almbladh and Pedroza, on the other hand, showed it to be singular there.
Additional work on light atoms show it to be either finite or to diverge at the
nucleus. For the determination of its structure for few-electron molecular systems
such as $H_2$ and $LiH$, the potential energy $v_{ee}(r)$ is assumed finite at each nucleus.
Expressions for $v_{ee}(r)$ at a nucleus have also been derived, but once again they are
based on the assumption that it is finite there. In various approximations with KS-DFT,
the potential energy $v_{ee}(r)$ also diverges at the nucleus.

The controversy was resolved for closed shell atoms and open shell atoms in the central
field approximation by Qian and Sahni who proved analytically that $v_{ee}(r)$ is in fact
finite at the nucleus. Furthermore, they were the first to show that this finiteness was a
direct consequence of the electron-nucleus cusp condition. In their proof they employed
the differential form of the cusp condition. In this form of the cusp condition, the angular
dependence is integrated out. Hence, its application constrains their proof to spherically
symmetric systems.

In this paper we generalize the conclusion of Qian and Sahni and prove that $v_{ee}(r)$ is finite
at a nucleus independent of the type of system (atomic, molecular, or solid state), and of
the system state and symmetry. Our proof employs instead the integrated form of the cusp
condition, and it is for this reason that the result is valid for systems of arbitrary symmetry.
The proof too is distinctly different. *Ex post facto*, the proof thus provides justification for all
the work on the determination of $v_{ee}(r)$ based on the assumption that it is finite at a nucleus.

It is also possible to transform the Schrödinger equation to that of the B system of
noninteracting bosons such that the density $\rho(r)$ and energy $E$ of the interacting system is
once again obtained. In this local effective potential energy theory, the density amplitude
\( \sqrt{\rho(r)} \) is determined directly. The differential equation for the model bosons is

\[
\left[-\frac{1}{2} \nabla^2 + v_B(r)\right] \sqrt{\rho(r)} = \mu \sqrt{\rho(r)},
\]

(9)

where \( v_B(r) \) is their effective potential energy:

\[
v_B(r) = v(r) + v_{ee}^B(r),
\]

(10)

with \( v_{ee}^B(r) \) the corresponding effective electron-interacting potential energy. The potential energy \( v_{ee}^B(r) \) accounts for Pauli and Coulomb correlations, and Correlation-Kinetic effects due to the difference in kinetic energy of the interacting fermion and noninteracting boson systems \[21\]. Once again, within density functional theory, \( v_{ee}^B(r) \) is defined \[8\] as a functional derivative of an electron-interaction energy functional \( E_{ee}^B[\rho] \), whereas in Q-DFT \[21\] it is the work done in a conservative field \( F_B(r) \). The energy is determined from the total energy functional or in terms of the components of the conservative field. The single eigenvalue \( \mu \) is the chemical potential or the negative of the ionization energy.

In this paper we also prove that the potential energy \( v_{ee}^B(r) \) is finite at a nucleus. The proof is again general and valid for systems of arbitrary state and symmetry, and also employs the integrated form of the cusp condition.

As a second component to the paper, we demonstrate the criticality of the electron-nucleus cusp condition to the finiteness of the potential energies \( v_{ee}(r) \) and \( v_{ee}^B(r) \) at a nucleus by application to the Hydrogen molecule. It becomes evident thereby that densities derived from wave functions that do not satisfy the cusp condition lead to potential energies that are singular at a nucleus, irrespective of how accurate the wave functions may be from an energy standpoint.

II. CRITICALITY OF CUSP CONDITION—APPLICATION TO THE HYDROGEN MOLECULE

For two electron systems in their ground state such as the Helium atom, Hooke’s atom, and Hydrogen molecule, the S and B systems are equivalent. This is because the S system
orbital is then \( \phi_i(r) = \sqrt{\rho(r)/2}, i = 1, 2 \). Hence, the demonstration of the significance of the cusp condition as applied to the Hydrogen molecule is equally valid for both systems. Inverting equations (9) or (6), we then have for the Hydrogen molecule

\[
v_{ee}(r) = v_{ee}^B(r) = \mu + \frac{\nabla^2 \sqrt{\rho(r)}}{2 \sqrt{\rho(r)}} - v(r). \tag{11}
\]

(In this example, the S system differential equation has only one eigenvalue.) It is evident, therefore, that the singularity in \( v(r) \) at each nucleus must be cancelled by the \( \frac{\nabla^2 \sqrt{\rho(r)}}{2 \sqrt{\rho(r)}} \) term in order for \( v_{ee}(r) \) or \( v_{ee}^B(r) \) to be finite there.

In our calculations we employ the accurate gaussian geminal wave function of Komasa and Thakkar \[22\] for the Hydrogen molecule which is spin free and of the form

\[
\psi(r_1, r_2) = \frac{1}{4}(1 + \hat{P}_{12})(1 + \hat{P}_{ab}) \sum_{k=1}^{150} c_k \phi_k \tag{12}
\]

in which

\[
\phi_k = \exp(-\alpha_k |r_1 - R_a|^2 - \beta_k |r_1 - R_b|^2 - \zeta_k |r_2 - R_a|^2 - \eta_k |r_2 - R_b|^2 - \gamma_k |r_1 - r_2|^2), \tag{13}
\]

where \( r_j \) for \( j \in \{1, 2\} \) are the position vector of the electrons, \( R_j \) for \( j \in \{a, b\} \) are the position vectors of the nuclei, \( \hat{P}_{12} \) and \( \hat{P}_{ab} \) are permutation operators that interchange the electronic and nuclear coordinates, respectively, and \( c_k, \alpha_k, \beta_k, \zeta_k, \eta_k, \gamma_k \) are variationally determined parameters subject to the square-integrability constraint

\[
(\alpha_k + \beta_k)(\eta_k + \zeta_k) + \gamma_k(\alpha_k + \beta_k + \eta_k + \zeta_k) > 0 \tag{14}
\]

for each \( k \). The individual exponential parameters are allowed to become negative as long as square-integrability is satisfied. The ground state energy obtained with this wave function is \( E = -1.174475313 \) a. u. and that of the most accurate correlated wave function \[23\] is \( E = -1.174475668 \) a.u. Thus the energy obtained by the gaussian wave function is accurate to the sixth decimal place. It is well known that such gaussian geminal or orbital wave functions do not satisfy the electron-nucleus cusp condition, and it is for this reason we employ this wave function. Additionally, in contrast to wave functions such as the Kolos-Roothan type wave function \[23, 24\], the calculations are analytical.
In Fig. 1 we plot the density along the nuclear bond axis with the two nuclei on the z axis at \( R = \pm 0.7 a.u. \). It is evident that the density is very accurate right up to the nucleus, and on the scale of the figure appears to possess a cusp at each nuclear position. However, in magnifying the scale as in Fig. 2, we see that there is no cusp as expected, and that the density is smooth across the nucleus.

In Fig. 3 we plot \( v(r) \) and \( \nabla^2 \sqrt{\rho(r)}/2\sqrt{\rho(r)} \) along the z axis about one nucleus. Whereas \( v(r) \) is singular as expected, the \( \nabla^2 \sqrt{\rho(r)}/2\sqrt{\rho(r)} \) term is finite at the nucleus. Therefore, the singularity in \( v(r) \) is not cancelled. Hence, although the wave function is very accurate from the perspective of the ground state energy, the fact that it does not satisfy the electron-nucleus cusp condition leads to the potential energy \( v_{ee}(r) \) (or \( v^B_{ee}(r) \)) being singular at each nucleus. In determining these potential energies from accurate densities, it is therefore imperative that the densities be obtained from wave functions that satisfy the electron-nucleus cusp condition.

**III. PROOF**

We first prove that the potential energy \( v_{ee}(r) \) is finite at a nucleus. Employing the integrated form of the electron-nucleus cusp condition for the wave function Eq. (5), the electron density near a nucleus as obtained from the definition of Eq. (4) is

\[
\rho(r) = \rho(0)[(1 - Zr)^2 + 2(1 - Zr)\sum_{k=1}^{3} B_k r_k + \sum_{l=1, m=1}^{3} r_l r_m A_{lm} + ...],
\]

where \( B_k = \int a_k \psi(0, \mathbf{r}_2, ..., \mathbf{r}_N)^{-1} d\mathbf{r}_2...d\mathbf{r}_N \) and \( A_{lm} = \int a_l a_m \psi(0, \mathbf{r}_2, ..., \mathbf{r}_N)^{-2} d\mathbf{r}_2...d\mathbf{r}_N \) are constants, and \( r_k, a_k \) etc., components of the vector \( \mathbf{r} \) and \( \mathbf{a} \). It follows then that

\[
\sqrt{\rho(r)} = \sqrt{\rho(0)[(1 - Zr)^2 + 2(1 - Zr)\sum_{k=1}^{3} B_k r_k + \sum_{l=1, m=1}^{3} r_l r_m A_{lm} + ...]}^{1/2}
\]

\[
= \sqrt{\rho(0)[1 - Zr + \mathbf{B} \cdot \mathbf{r} + O(r^2)]},
\]

where in the second step we have retained only terms of \( O(r) \).

Inverting the S system differential equation we obtain for any occupied orbital \( \phi_i(r) \) the
FIG. 1: The electron density $\rho(r)$ of the Hydrogen molecule along the nuclear bond axis in atomic units (a.u.). The nuclei are on this axis at $\pm 0.7a.u.$ The density is determined by the wave function of Eq.(12).

expression for the electron-interaction potential energy $v_{ee}(r)$ as

$$v_{ee}(r) = \epsilon_i + \frac{\nabla^2 \phi_i(r)}{2\phi_i(r)} - v(r).$$  \hspace{1cm} (17)

Next, we rewrite the orbitals $\phi_i(r)$ as

$$\phi_i(r) = \sqrt{\rho(r)c_i(r)}, \; i = 1, 2, \ldots N,$$  \hspace{1cm} (18)

where the coefficients $c_i(r)$ satisfy

$$\sum_{i=1}^{N} c_i(r)^2 = 1.$$  \hspace{1cm} (19)

This definition of the $\phi_i(r)$ is consistent with Eq. (8). Expanding the coefficient $c_i(r)$ about
the nucleus we obtain

\[ c_i(r) = c_i(0) + \nabla c_i(0) \cdot r + O(r^2) \]
\[ = c_i(0)[1 + D \cdot r + O(r^2)], \quad (20) \]

where \( D = \nabla c_i(0)/c_i(0) \) is some constant vector. Inserting Eq. (16) and (20) into Eq. (18), we obtain the expression for the orbitals \( \phi_i(r) \) near the nucleus as

\[ \phi_i(r) = \sqrt{\rho(0)c_i(0)[1 - Zr + (B + D) \cdot r + O(r^2)]}. \quad (21) \]
FIG. 3: The external potential energy $v(r)$ and the function $\frac{\nabla^2 \sqrt{\rho(r)}}{2\sqrt{\rho(r)}}$ about a nucleus of the Hydrogen molecule in atomic units (a.u.). The density $\rho(r)$ is determined by the wave function of Eq. (12). The singularity of the external potential energy at the nucleus is not cancelled by the $\frac{\nabla^2 \sqrt{\rho(r)}}{2\sqrt{\rho(r)}}$ function.

Now the expression for the external potential energy near the nucleus is

$$v(r) = -\frac{Z}{r} - \sum'_{\alpha} \frac{Z}{|r-R_\alpha|},$$

where the sum is over all the other nuclei. At the nucleus, the term $-\frac{Z}{r}$ is singular, whereas the other terms are constants. From Eq. (17) it is evident that this singularity must be cancelled by the $\frac{\nabla^2 \phi_{i}(r)}{2\phi_{i}(r)}$ term.
Consider the term $\frac{\nabla^2 \phi_i(r)}{2\phi_i(r)}$ near the nucleus with $\phi_i(r)$ given by Eq. (21). We have $\nabla^2 r = 2/r$ and $\nabla^2 (B + D) \cdot r = 0$. After acting by $\nabla^2$ and taking the limit as $r \to 0$, terms of $O(r^2)$ lead to constants while higher order terms vanish. Thus, near the nucleus, the term $\frac{\nabla^2 \phi_i(r)}{2\phi_i(r)}$ is $-Z/r$ plus some constant, and therefore in this limit the singularity of the external potential energy is cancelled. Therefore $v_{ee}(0)$ is finite.

The proof of the finiteness of the B system potential energy $v^B_{ee}(r)$ at the nucleus is along the same lines as above. Substitution of Eq.(16) into the expression for $v^B_{ee}(r)$ of Eq.(11) leads to the result that $v^B_{ee}(0)$ is finite. This result may also be arrived at as a special case of the S system proof for which $c_i = 1/\sqrt{N}$.

IV. CONCLUSION

We have proved that the effective electron-interaction potential energy of model noninteracting fermi and bose systems that reproduce the density and energy of an interacting fermi system in an external field is finite at a nucleus. The proof is valid for arbitrary state and symmetry of the interacting system. The finiteness of this potential energy at the nucleus in these local effective potential energy theories is a direct consequence of the electron-nucleus cusp condition. Since the cusp condition holds for both ground and excited states of the interacting system, the effective electron-interaction potential energy is finite at the nucleus whether the noninteracting fermions are in a ground or excited state. The proof is general, and does not distinguish between ground and excited states of the model system. The noninteracting bosons are, of course, always in their ground state.

The study of the structure of these effective potential energies via densities derived from accurate wave functions now has an important proviso. These wave functions must satisfy the electron-nucleus cusp condition. Otherwise, the potential energies will be singular at a nucleus, thereby leading to erroneous conclusions regarding their structure.
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