

# Elimination of Coulombic infinities through transformation of the Hamiltonian

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It is demonstrated that Coulombic infinities of both nuclear–electron and electron–electron type can be eliminated through a transformation of the Hamiltonian. The transformed Hamiltonian is no longer self-adjoint and will contain three-particle interactions. The new pair interaction, depending only on the interparticle distance, can be chosen almost at will, however. If the new pair-potential terms are chosen to not contain an infinity, the corresponding right-hand wave function no longer contains a cusp, and we expect this feature to help improve the convergence of *ab initio* quantum chemical calculations with respect to the one-particle basis set. We limit ourselves to an exposition of the idea, illustrated with some examples for the Hydrogen atom. © 1998 American Institute of Physics. [S0021-9606(98)01743-7]

## I. INTRODUCTION

Due to infinities in the Coulombic interparticle interactions, the exact wave function generally has a cusp whenever the coordinates of two particles coincide (e.g., Refs. 1–5). This is most trivially seen by inspecting the quantity

$$\frac{\hat{H}\Psi}{\Psi} = \frac{\hat{T}\Psi}{\Psi} + V = E. \quad (1)$$

If the potential  $V$  tends to  $\pm\infty$ , the local kinetic energy  $\hat{T}\Psi/\Psi$  should tend to infinity in order to add to a finite sum  $E$ . This implies that the wave function has a cusp, unless it is zero. The above indicates that the Schrödinger equation is a rather ill-behaved numerical problem near the coalescence of two charged particles.

In the common practice of quantum chemistry, these problems are largely ignored. Gaussian atomic orbital basis sets are used overwhelmingly, and the resulting wave functions do not have a cusp at the nucleus and consequently  $\hat{H}\Psi/\Psi$  tends to  $-\infty$  near any nucleus. This does not necessarily lead to bad energies since the volume where the behavior is bad is very small. As essentially all of the basis sets used in quantum chemistry contain functions that explicitly depend on the electron–nuclear distance, this helps to incorporate a more reliable description of the nuclear cusp or alternatively, the local kinetic energy, particularly when large exponent Gaussians are included in the basis.<sup>6</sup>

The electron–electron cusp is more worrisome. The overwhelming majority of quantum chemical calculations make the approximation of expanding many-electron wave functions in antisymmetrized products of one-particle functions (determinants). Therefore, there is no explicit dependence on the electron–electron distance, and electron correlation has to be included through a large expansion of determinants. In addition (and presumably relatedly), the

convergence of the energy with respect to the one-particle basis set is notoriously bad. This has been attributed to the electron cusp (e.g., Ref. 7). The exact cusp condition is of the form

$$\frac{\partial\Psi(r_1, r_2, r_{12})}{\partial r_{12}} = \eta\Psi(r_{12}=0), \quad (2)$$

where  $\eta$  is  $\frac{1}{2}$ ,  $\frac{1}{4}$ , or  $\frac{1}{6}$  depending on symmetry of the wave function under exchange and inversion. It is never zero,<sup>7</sup> while for any quantum chemical wave functions composed of product of one-particle functions,  $\partial\Psi(r_{12})/\partial r_{12}=0$  [This point was emphasized to us by Professor John Morgan, private communication]. Trial functions that explicitly depend on the electronic distance are capable of yielding much more rapidly converging expansions [Hylleraas configuration interaction (CI),<sup>8–13</sup> Jastrow functions,<sup>14</sup> Gaussian Geminal expansions,<sup>15–19</sup> explicitly correlated coupled cluster (CC) and many-body perturbation theory (MBPT)<sup>20–23</sup>], because they have an infinite or at least large local kinetic energy at an electron–electron coalescence.

Traditionally, methods in quantum chemistry [disregarding density functional theory (DFT)] focus on obtaining a more and more accurate wave function, usually depending upon the variational principle. Alternatively, nonvariational methods like coupled-cluster theory and its equation-of-motion (EOM) generalizations,<sup>24,25</sup> or complex scaling methods,<sup>26</sup> suggest alternative approaches that lead to transformed Hamiltonians. Here, let us consider a two-step approach. We first modify the problem to an equivalent one that is more amenable to numerical solution. In the present case we can think of two (related) possibilities. We can represent the exact wave function as

$$|\Psi\rangle = \hat{X}|\Phi\rangle, \quad (3)$$

where  $\hat{X}$  is as of yet an unspecified, but fixed operator. Applying the variational principle to

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$$E = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \frac{\langle \Phi | \hat{X}^\dagger \hat{H} \hat{X} | \Phi \rangle}{\langle \Phi | \hat{X}^\dagger \hat{X} | \Phi \rangle}, \quad (4)$$

we have the following equation for  $|\Phi\rangle$

$$(\hat{X}^\dagger \hat{H} \hat{X})|\Phi\rangle = \hat{X}^\dagger \hat{X}|\Phi\rangle E. \quad (5)$$

Hence the Schrödinger eigenvalue problem is transformed into a generalized eigenvalue problem involving a transformed Hamiltonian and a metric  $\hat{S} = \hat{X}^\dagger \hat{X}$ . The other approach is obtained if we multiply the above equation on the left by the inverse metric (assuming it exists), to obtain

$$(\hat{X}^{-1} \hat{H} \hat{X})|\Phi\rangle = |\Phi\rangle E. \quad (6)$$

Hence the Hamiltonian is transformed by the operator  $\hat{X}$  and the Schrödinger equation is transformed into a (in general) nonself-adjoint eigenvalue problem. The metric and similarity transform approaches are closely related, and they are completely equivalent if the operator  $\hat{X}$  is unitary, implying that the metric is unity.

In the above we have disregarded the issue of boundary conditions. The usual Schrödinger equation is subject to the boundary condition that a solution  $|\Psi\rangle$  is part of Hilbert space. Since we have the mapping  $\hat{X}|\Phi\rangle = |\Psi\rangle$ , a different boundary condition is associated with Eq. (5), namely that  $\hat{X}|\Phi\rangle$  should be part of Hilbert space. The solutions  $|\Phi\rangle$  themselves may have a component outside of Hilbert space. Under these conditions we have a direct mapping from the original problem to the transformed problem, demonstrating that the eigenvalues do not change. Therefore, under the changed boundary condition, the eigenvalues of Eq. (5) are all real and identical to the solutions of the original problem. This rather delicate issue can be illustrated by examining the textbook solution for the Hydrogen atom. Transforming the Hamiltonian with the ground state of the Hydrogen atom leads to  $\hat{H} = e^r \hat{H} e^{-r}$  and one obtains the Laguerre polynomials  $L_n(r)$  as solutions of the non-Hermitian transformed radial Hamiltonian. The Laguerre polynomials are not square integrable, but the back transformed functions  $e^{-r} L_n(r)$  are.

This example also illustrates another aspect of the similarity transform approach, namely that the left and right hand eigenfunctions are no longer adjoints. The left hand eigenfunctions in the case of the Hydrogen atom discussed above are given by  $L_n(r)e^{-2r}$ . It is seen that the unboundedness of the right hand wave function is corrected by the left hand wave function. ‘‘Expectation values’’ are to be evaluated as transition matrix elements between corresponding left and right hand states, and the inner product of the left and right hand state is properly normalizable.

Let us surmise that in practical quantum chemical calculations, the basis set expansions are such that the obtained wave functions are always trivially square integrable. We have in mind to use similar expansions for the transformed wave functions  $|\Phi\rangle$ , and this may put some restrictions on possible operators  $\hat{X}$ , as we will want  $|\Phi\rangle$  to be part of Hilbert space. After this digression let us proceed.

The operator  $\hat{X}$  in principle can have many forms. In the realm of highly intense laser fields, for example, the so-called Bloch–Nordsiek transformation<sup>27</sup> is frequently em-

ployed, which acts as a translation operator and contains the momentum operator as the generator of this translation.<sup>28</sup> This allows one to ‘‘replace’’ the interaction of particles and the field through dressed interactions between the particles and modified canonical variables for the field.

Here we will restrict ourselves to the case that  $\hat{X}$  is a simple many-particle multiplicative operator (that is, simply a function), depending on all of the particle coordinates. This function is taken to be symmetric under interchange of the coordinates of identical particles, in order not to change this same symmetry of the Hamiltonian. Moreover we require the function  $X$  to be nonzero, in order to not introduce any trouble with  $X^{-1}$ . Thus, the simplest parametrization is to use  $X = e^G$  where  $G$  is in principle an arbitrary function of the particle coordinates, symmetric under interchange of the coordinates of identical particles. Through the transformation with  $e^G$ , we want to introduce the explicit dependence on the interparticle distances in the exact wave function  $\Psi = e^G \Phi$ . Such an approach has been considered before in the trans-correlation method of Boys and Handy in the late sixties.<sup>29–32</sup> In the trans-correlation approach, the free parameters in the function  $G$  (of predetermined form) were optimized. Such a nonlinear optimization procedure is rather horrific numerically and not easily made efficient on present-day computers.

Our point of departure is different. We will choose the function  $G$  once and for all and focus on the properties of the transformed Hamiltonian  $\tilde{H} = e^{-G} \hat{H} e^G$ . Our goal is to eliminate the Coulombic singularities (Strictly speaking the transformed interaction is finite everywhere, but its derivatives can still contain singular points.) from the Hamiltonian, at the same time keeping the problems of non-Hermiticity and, as we shall see below, the occurrence of three-particle interactions under control. The hope is that this should lead to a numerically more stable problem and more smoothly varying solutions  $\Phi$  than in the original Schrödinger eigenvalue problem. The function  $\Phi$  can be solved for in a variety of more or less conventional ways, but we would expect an improved convergence behavior. Hirschfelder<sup>33</sup> has long ago proposed this approach to eliminate the electron–electron cusp, considering one special form for the transforming function, but to our knowledge no numerical results have ever been presented. Interestingly this approach has been pursued independently<sup>34</sup> to eliminate the electron–nuclear cusp, using Hirschfelder’s transforming function, in the context of plane-wave-based density functional theory. Numerical results were presented but the authors found it hard to gauge the improvement of their results.

In the next section we will assume the simplest possible form for  $G$

$$G = \sum_{i < j} g_{ij}(r_{ij}). \quad (7)$$

The elementary geminal functions  $g_{ij}$  depend on the distance between particles  $i$  and  $j$  only and, of course, on the type of particles involved. Assuming this form for the transformation, we will derive the general form of the transformed

Hamiltonian in very simple format. We will show that the new two-particle interactions can be chosen to not contain an infinity, essentially when

$$\frac{dg_{ij}(r_{ij})}{dr_{ij}} \neq 0, \quad (8)$$

which is an almost trivial condition. This allows an enormous freedom for the choice of the geminal functions  $g_{ij}$ . This freedom can be used to mold the Hamiltonian into a most favorable form. In these initial investigations, we will simply outline a number of possibilities. In Sec. III we analyze the situation for the simple case of two charged particles. The Hydrogen atom serves as the prototypical example, but the treatment of electron–electron interactions is completely analogous. A survey of possibilities and potential problems is provided in Sec. IV.

## II. TRANSFORMATION OF THE MANY-PARTICLE HAMILTONIAN

Let us consider the general nonrelativistic Hamiltonian with Coulombic interactions between the particles

$$\hat{H} = \hat{T} + \hat{V} = -\frac{1}{2} \sum_i \frac{1}{m_i} \nabla_i^2 + \frac{1}{2} \sum_{i \neq j} \frac{q_i q_j}{|\mathbf{r}_i - \mathbf{r}_j|}, \quad (9)$$

where  $m_i$  indicates the mass and  $q_i$  denotes the charge of particle  $i$ , in atomic units. We will consider a transformation of the Hamiltonian with the multiplicative operator  $e^G$ , where  $G$  is a symmetric sum of two-particle geminals that each depend only on the relevant interparticle distance  $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ . Hence

$$G = \frac{1}{2} \sum_{i \neq j} g_{ij}(r_{ij}). \quad (10)$$

We will henceforth suppress the indices on the geminal(s)  $g$ , to facilitate the notation. The transformed Hamiltonian can be written

$$\hat{\tilde{H}} = e^{-G} \hat{H} e^G = \hat{H} + [\hat{T}, G] + \frac{1}{2} [[\hat{T}, G], G], \quad (11)$$

since  $V$  commutes with  $G$ . Higher order commutators do not occur since  $\hat{T}$  is a second-order differential operator. The commutators can be evaluated as

$$\begin{aligned} [\hat{T}, G] &= -\frac{1}{2} \sum_{i, k \neq l} \frac{1}{2m_i} (\nabla_i^2 g(r_{kl}) + 2(\nabla_i g(r_{kl})) \cdot \nabla_i) \\ &= -\frac{1}{4} \sum_{i \neq j} \left[ \frac{1}{m_i} (\nabla_i^2 g(r_{ij})) + \frac{1}{m_j} (\nabla_j^2 g(r_{ij})) \right] \\ &\quad - \frac{1}{2} \sum_{i \neq j} \left[ \frac{1}{m_i} (\nabla_i g(r_{ij})) \cdot \nabla_i + \frac{1}{m_j} (\nabla_j g(r_{ij})) \cdot \nabla_j \right]. \end{aligned} \quad (12)$$

Using that  $g(r_{ij})$  is a function of the interparticle distance only, we find

$$\nabla_i g(r_{ij}) = -\nabla_j g(r_{ij}) = \frac{dg(r_{ij})}{dr_{ij}} \frac{\mathbf{r}_i - \mathbf{r}_j}{r_{ij}} \equiv g'(r_{ij}) \frac{\mathbf{r}_i - \mathbf{r}_j}{r_{ij}}, \quad (13)$$

$$\begin{aligned} \nabla_i^2 g(r_{ij}) &= \nabla_j^2 g(r_{ij}) = \frac{2}{r_{ij}} \frac{dg(r_{ij})}{dr_{ij}} + \frac{d^2 g(r_{ij})}{d^2 r_{ij}} \\ &= \frac{2}{r_{ij}} g'(r_{ij}) + g''(r_{ij}). \end{aligned} \quad (14)$$

Hence

$$\begin{aligned} [\hat{T}, G] &= -\frac{1}{4} \sum_{i \neq j} \left( \frac{1}{m_i} + \frac{1}{m_j} \right) \left[ \frac{2}{r_{ij}} g'(r_{ij}) + g''(r_{ij}) \right] \\ &\quad - \frac{1}{2} \sum_{i \neq j} g'(r_{ij}) \frac{\mathbf{r}_i - \mathbf{r}_j}{r_{ij}} \cdot \left( \frac{1}{m_i} \nabla_i - \frac{1}{m_j} \nabla_j \right). \end{aligned} \quad (15)$$

Introducing the reduced mass

$$\frac{1}{\mu_{ij}} = \frac{1}{m_i} + \frac{1}{m_j} \quad (16)$$

or

$$\mu_{ij} = \frac{m_i m_j}{m_i + m_j}, \quad (17)$$

we can write

$$\begin{aligned} [\hat{T}, G] &= -\frac{1}{2} \sum_{i \neq j} \left[ \frac{1}{\mu_{ij} r_{ij}} g'(r_{ij}) + \frac{1}{2\mu_{ij}} g''(r_{ij}) \right] \\ &\quad - \frac{1}{2} \sum_{i \neq j} g'(r_{ij}) \frac{\mathbf{r}_i - \mathbf{r}_j}{r_{ij}} \cdot \left( \frac{1}{m_i} \nabla_i - \frac{1}{m_j} \nabla_j \right). \end{aligned} \quad (18)$$

The single commutator, therefore, consists of a multiplicative two-particle potential and a velocity dependent interaction which, in general, is not self-adjoint.

Similarly the double commutator can be written

$$\begin{aligned} \frac{1}{2} [[\hat{T}, G], G] &= -\frac{1}{16} \sum_{k, i \neq m, j \neq n} \frac{2}{m_k} (\nabla_k g(r_{im}) \cdot \nabla_k g(r_{jn})) \\ &= -\frac{1}{2} \sum_{k \neq i, k \neq j} \frac{1}{m_k} (\nabla_k g(r_{ki}) \cdot \nabla_k g(r_{kj})) \\ &= -\frac{1}{2} \sum_{k \neq i, k \neq j} \frac{1}{m_k} g'(r_{ki}) g'(r_{kj}) \frac{(\mathbf{r}_k - \mathbf{r}_i)}{r_{ki}} \\ &\quad \cdot \frac{(\mathbf{r}_k - \mathbf{r}_j)}{r_{kj}} = -\frac{1}{2} \sum_{k \neq i} \frac{1}{m_k} (g'(r_{ki}))^2 \\ &\quad - \frac{1}{2} \sum_{k \neq i \neq j} \frac{1}{m_k} g'(r_{ki}) g'(r_{kj}) \frac{(\mathbf{r}_k - \mathbf{r}_i)}{r_{ki}} \\ &\quad \cdot \frac{(\mathbf{r}_k - \mathbf{r}_j)}{r_{kj}}, \end{aligned} \quad (19)$$

where, in going to the last line, the term is split in a ‘‘diagonal’’ contribution  $i = j$ , and a remaining true three-particle contribution. The two-particle contribution is more conveniently written in a symmetric way as

$$\begin{aligned}
 -\frac{1}{2} \sum_{k \neq i} \frac{1}{m_k} (g'(r_{ki}))^2 &= -\frac{1}{4} \sum_{i \neq j} \left( \frac{1}{m_i} + \frac{1}{m_j} \right) (g'(r_{ij}))^2 \\
 &= -\frac{1}{2} \sum_{i \neq j} \frac{1}{2\mu_{ij}} (g'(r_{ij}))^2.
 \end{aligned}
 \tag{20}$$

Collecting terms, the transformed Hamiltonian can be written as

$$\hat{H} = \hat{T} + \hat{A} + \hat{V}_2 + \hat{V}_3,
 \tag{21}$$

where

$$\hat{T} = -\frac{1}{2} \sum_i \frac{\nabla_i^2}{m_i}
 \tag{22}$$

is the usual kinetic energy operator

$$\hat{A} = -\frac{1}{2} \sum_{i \neq j} g'(r_{ij}) \frac{\mathbf{r}_i - \mathbf{r}_j}{r_{ij}} \cdot \left( \frac{\nabla_i}{m_i} - \frac{\nabla_j}{m_j} \right),
 \tag{23}$$

is a two-particle, in general nonself-adjoint, velocity-dependent potential or drift term

$$\hat{V}_2 = \frac{1}{2} \sum_{i \neq j} \left[ \frac{q_i q_j}{r_{ij}} - \frac{g'(r_{ij})}{\mu_{ij} r_{ij}} - \frac{g''(r_{ij}) + (g'(r_{ij}))^2}{2\mu_{ij}} \right],
 \tag{24}$$

is a modified multiplicative two-particle potential, and finally

$$\hat{V}_3 = -\frac{1}{2} \sum_{k \neq i \neq j} \frac{g'(r_{ki}) g'(r_{kj})}{m_k} \frac{(\mathbf{r}_k - \mathbf{r}_i)}{r_{ki}} \cdot \frac{(\mathbf{r}_k - \mathbf{r}_j)}{r_{kj}},
 \tag{25}$$

is a true three-particle, multiplicative, potential term.

The above result has interesting implications. The above transformation shows that we can, within limits, pick any two-particle interaction we want. The price to pay is an introduction of three-particle interactions, and a velocity-dependent term. In addition we note the term  $(\mathbf{r}_i - \mathbf{r}_j)/r_{ij}$  has a discontinuity near  $\mathbf{r}_i = \mathbf{r}_j$ .<sup>33</sup> As mentioned before, in general the transformed Hamiltonian is no longer self-adjoint and this may pose some fundamental problems. If the chosen transformation is not bounded, the eigenfunctions of the transformed Hamiltonian may no longer be square integrable. The variational principle in quantum mechanics has to be replaced by a bivariational principle, implying that one gets both left- and right-hand wave functions. In the approach described above, only the right-hand wave function becomes simpler as it no longer contains a cusp. The left-hand eigenfunctions will actually become more cumbersome to calculate. Similar problems arise in the treatment of resonances through the method of complex scaling. A very readable account of these difficult topics has been presented by Löwdin.<sup>35</sup> Let us emphasize that the exact eigenvalues of the transformed Hamiltonian do not change (provided the boundary conditions are transformed accordingly, see introduction). However, if the Hamiltonian is mapped onto a finite basis, the resulting nonsymmetric Hamiltonian may have certain complex eigenvalues. Complex eigenvalues may be an indication that the basis set is insufficient to describe the corresponding state.

The transformed Hamiltonian is self-adjoint only if the function  $G$  is purely imaginary, since then the transformation is norm-conserving and unitary. However, it does not seem possible to eliminate the Coulombic infinity through such a transformation. It is possible to define a general complex transformation, but since this does not render the transformed Hamiltonian self-adjoint, this also does not seem very useful. We will limit ourselves to real-valued functions.

Up to now our discussion has been fairly general. Our only assumption has been the form of the transformation. It is time to consider feasible choices for the geminals  $g_{ij}$ , that in general will depend on the type of particles. Let us establish some desiderata that have to be satisfied by our new Hamiltonian. The purpose of the transformation is to eliminate the infinity from the two-particle potential. The most obvious way to accomplish this is to require that

$$\frac{q_i q_j}{r_{ij}} - \frac{g'(r_{ij})}{\mu_{ij} r_{ij}},
 \tag{26}$$

is regular at the origin. This will be satisfied provided

$$\lim_{r_{ij} \rightarrow 0} g'(r_{ij}) = q_i q_j \mu_{ij}.
 \tag{27}$$

This is a very trivial condition. As long as a function  $g(r_{ij})$  has a nonzero derivative at the origin, it can always be scaled to satisfy Eq. (27). We do have to worry about the new velocity-dependent term and the three-particle interactions. In particular we note that

$$\frac{\mathbf{r}_i - \mathbf{r}_j}{r_{ij}},
 \tag{28}$$

does not fall off with the interparticle distance. Therefore we have to require that the functions  $g'(r_{ij})$  (as well as  $g''(r_{ij})$ ) fall off rather rapidly with the interparticle distance. This is important to reduce the degree of non-Hermiticity of the Hamiltonian. In addition it will reduce the effective range of the three-particle interactions.

For this reason the most obvious choice for the geminal  $g$

$$g(r_{ij}) = q_i q_j \mu_{ij} r_{ij},
 \tag{29}$$

does not seem practical. Interestingly, this choice eliminates the Coulomb potential entirely. The two-particle interaction is reduced to a constant term

$$V_2 \rightarrow -\frac{1}{2} \sum_{i < j} q_i^2 q_j^2 \mu_{ij}.
 \tag{30}$$

However, the three-particle potential, as well as the velocity-dependent part, has infinite range (and the transformation is unbounded). As an aside, the explicitly correlated CC method (CCR12) of Noga, Klopper, and Kutzelnigg<sup>36</sup> uses the pure excitation part of the operator  $r_{ij}$  in an exponential ansatz. There are some additional parameters in this scheme and it seems that these are needed to overcome the potential improper behavior of this parameterization if the electrons are far apart. This observation may provide some additional insight in the workings of the CCR12 method.<sup>23,36</sup>

### III. ANALYSIS OF HYDROGEN-LIKE SYSTEMS

In order to analyze potential candidates for the geminal function  $g(r)$ , it is illustrative to first consider the simplest possible Coulombic system, namely the hydrogen-like atom consisting of an electron and a nucleus with charge  $Z$ . The new electron–nuclear interaction potential is given by

$$V(r) = -\frac{Z}{r} - \frac{g'(r)}{\mu r} - \frac{g''(r)}{2\mu} - \frac{(g'(r))^2}{2\mu}. \quad (31)$$

The three-particle potential is absent, of course, and the radial part of the velocity-dependent potential is given by

$$A = g'(r) \frac{d}{dr}. \quad (32)$$

The total radial part of the new Schrödinger equation reads

$$\frac{1}{\mu r} \frac{d\varphi}{dr} + \frac{1}{2\mu} \frac{d^2\varphi}{dr^2} + V(r)\varphi(r) + g'(r) \frac{d\varphi}{dr} = E\varphi(r). \quad (33)$$

This equation is correct only for spherical ( $l=0$ ) solutions. After choosing a geminal  $g(r)$ , it is not necessary to explicitly solve for the ground state of the transformed problem because the (unnormalized) solution is given immediately as

$$\varphi(r) = e^{-g(r)} \psi(r) = e^{-g(r)} e^{-\mu Z r}, \quad (34)$$

where  $\psi(r)$  is the ground state of the original radial Schrödinger equation. In Table I below, we list a few elementary functions  $g(r)$  together with the potentials they generate, and the derivative  $g'(r)$ . The common factor  $-Z\mu$ , which in the more general case would read  $q_i q_j \mu_{ij}$ , is abbreviated as

$Q\mu$ . Therefore, these potentials apply for the general Coulomb problem, including the interactions between two electrons. The potentials in Table I contain some arbitrary parameters, for which suitable values are to be chosen. These parameters are listed in Table I. In addition, in the last column of Table I, we include the value of the potential in the limit  $r \rightarrow 0$ . In Figs. 1(a)–6(a), we plot the potentials for three reasonable and illustrative values of the parameters (where reasonable means that the potentials do not deviate too much from the original Coulomb potential, also drawn in the figures). In Figs. 1(b)–6(b) we have drawn the corresponding exact, but unnormalized, wave function [Eq. (34)] that would result from solving the respective radial Schrödinger equation. From these plots we conclude that, in particular, potentials III, VI, VII, and VIII appear to yield wave functions that can be well represented in terms of an expansion in Gaussian atomic basis functions. Another important criterion is the feasibility of the integrals. Case VIII scores very well in this respect. It is defined in terms of the error function

$$g(r) = -\frac{\sqrt{\pi} Q\mu}{2D} \operatorname{erf}(-dr) = \frac{Q\mu}{D} \int_{-dr}^0 e^{-t^2} dt. \quad (35)$$

These integrals comply very well with the usual calculation of Gaussian integrals.

The prime reason to apply the transformation approach to the problem of the electron–nuclear cusp is the potential improvement of properties near the nucleus. Energetically one does not expect to gain too much, since Gaussian basis sets located on each atom are generally quite satisfactory. We have used transformation VIII in an otherwise standard

TABLE I. Examples of generating functions and resulting two-particle interactions.

#	$g(r)$	$g'(r)$	parameter	$v(r)$	$\lim_{r \rightarrow 0}(r)$
I	0	0	...	$Q/r$	$\infty$
II	$\mu Q r$	$\mu Q$	...	$-\frac{1}{2}\mu Q^2$	$-\frac{1}{2}\mu Q^2$
III	$\mu Q s \ln(s+r)$	$\frac{\mu Q s}{s+r}$	s	$\frac{Q}{s+r} + \frac{1}{2} \frac{Qs(1-\mu Qs)}{(s+r)^2}$	$\frac{3Q}{2s} - \frac{1}{2} Q^2 \mu$
IV	$\frac{\mu Q}{a} \arctan(ar)$	$\frac{\mu Q}{1+a^2 r^2}$	a	$\frac{Q a^2 r}{1+a^2 r^2} + \frac{1}{2} Q \frac{(2a^2 r - \mu Q)}{(1+a^2 r^2)^2}$	$-\frac{1}{2} Q^2 \mu$
V	$\mu Q r e^{-br^2}$	$(\mu Q - 2\mu Q b r^2) e^{-br^2}$	b	$\frac{Q(1-e^{-br^2})}{r} + (5Qbr - 2Qr^3 b^2) e^{-br^2}$ $+ \left( 2\mu Q^2 r^2 b - \frac{1}{2}\mu Q^2 - 2\mu Q^2 r^4 b^2 \right) e^{-2br^2}$	$-\frac{1}{2} Q^2 \mu$
VI	$-\mu Q c e^{-cr}$	$\mu Q e^{-cr}$	c	$\frac{Q(1-e^{-cr})}{r}$ $+ \frac{1}{2} Q c e^{-cr} - \frac{1}{2} \mu Q^2 e^{-2cr}$	$\frac{3}{2} Q c - \frac{1}{2} Q^2 \mu$
VII	$-\frac{Q\mu t^2}{(t+r)}$	$\frac{Q\mu t^2}{(t+r)^2}$	t	$\frac{Q(2t+r)}{(t+r)^2}$ $+ \frac{1}{2} Q t^2 \frac{(2t+2r-\mu Q t^2)}{(t+r)^4}$	$\frac{3}{t} - \frac{1}{2} Q^2 \mu$
VIII	$-\frac{\sqrt{\pi} Q\mu}{2d} \operatorname{erf}(-dr)$	$Q\mu e^{-d^2 r^2}$	d	$\frac{Q(1-e^{-d^2 r^2})}{r}$ $+ Q d^2 r e^{-d^2 r^2} - \frac{1}{2} \mu Q^2 e^{-2d^2 r^2}$	$-\frac{1}{2} Q^2 \mu$

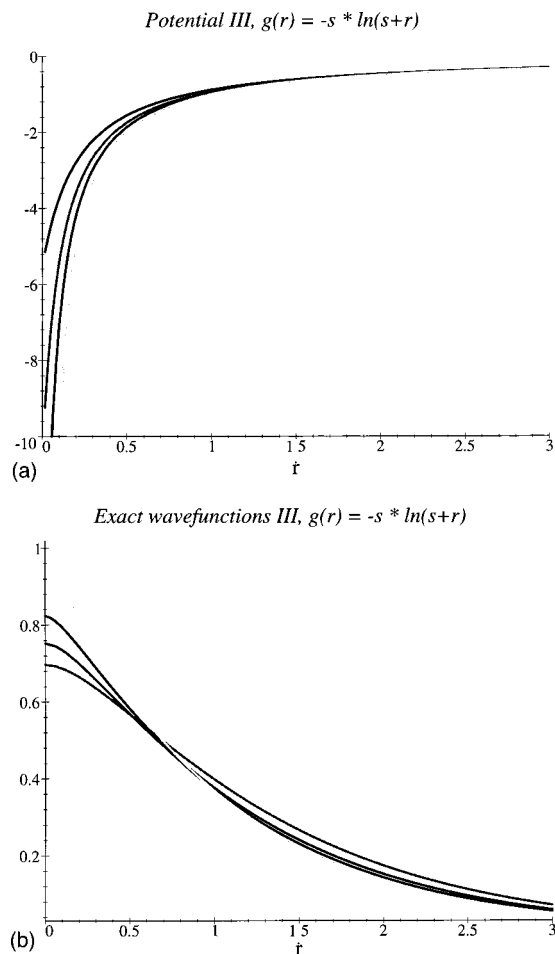


FIG. 1. (a) Potential III, generated by  $g(r) = -s \ln(s+r)$ . Included is the Coulomb potential  $-1/r$  and, in order of increasing closeness to  $-1/r$ ,  $V_{III}(r;s)$  for  $s=0.3$ ,  $s=0.15$ , and  $s=0.075$ . (b) Corresponding exact radial wave functions for same values of  $s$ , in addition to  $e^{-r}$ .

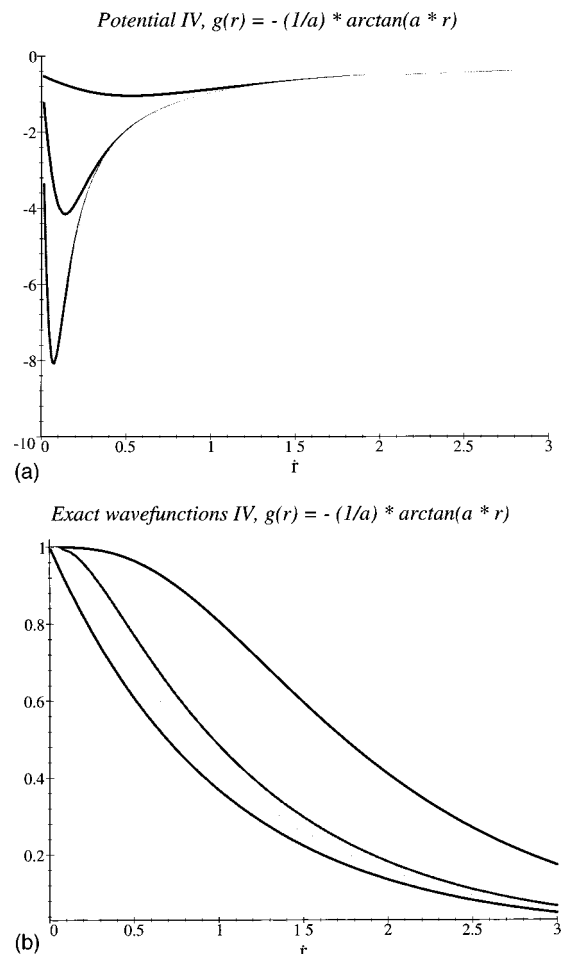


FIG. 2. (a) Potential IV, generated by  $g(r) = -(1/a) \arctan(a \cdot r)$ . Included is the Coulomb potential  $-1/r$  and, in order of closeness to  $-1/r$ ,  $V_{IV}(r;a)$  for  $a=10.0$ ,  $a=5.0$ , and  $a=1.0$ . (b) Corresponding exact radial wave functions for same values of  $a$ , in addition to  $e^{-r}$ .

3-Gaussian fit to Slater-type orbitals (STO-3G) basis-set calculation of the hydrogen atom. By varying the parameter  $d$ , the resulting energy brackets the exact energy of the hydrogen atom, hence the energy may be lower than the exact value. In Table II we have included a selection of results. From Table II we find that properties do not necessarily improve. Also we found (not shown) that extending the basis set most strongly improves properties for the normal Hamiltonian. Of course, one has to keep in mind that the basis sets used are optimized for the untransformed problem. However, the fact that the left-hand wave function, needed to obtain properties, actually has a stronger cusp and is poorly described in the Gaussian basis will play a role too. Our experience with the other transformations is similar.

The situation regarding the electron cusp is more complicated, since we want the wave function to be presentable in terms of a linear combination of products of one-particle functions. This is more difficult to analyze, also because exact many-particle wave functions are not known analytically. It seems a good idea to apply our transformation techniques to the Hooke's law model (for overviews see e.g., Refs. 37 and 38). This is a model two-electron system in which the nuclear-electron Coulomb potential is replaced by a har-

monic potential. This allows one to solve the problem analytically. The ground state is the so-called Kais function.<sup>39</sup> The analysis of this problem is beyond the scope of this paper. However, given the above results for hydrogen, it is pertinent to analyze this case in order to judge the potential of the scheme. Related approaches for treating Coulombic singularities have also been considered by Panas,<sup>40</sup> Taylor,<sup>41</sup> and Teter (private communication).

TABLE II. Energy and properties for the hydrogen atom calculated in STO-3G basis set.

Property	Exact	% deviation = 100*(exact-calculated)/exact		
		Pot. VIII $d=0.3$ (%)	Pot. VIII $q=0.4$ (%)	Normal Hamiltonian (%)
$E$	-0.5	0.19	-0.29	-0.85
$\bar{r}^{-1}$	1.0	1.52	0.96	0.32
$\bar{r}^2$	2.0	-2.22	-3.46	-4.88
$r$	1.5	-3.84	-3.49	-3.08
$r^2$	3.0	-10.04	-9.51	-8.86
$\delta(r)$	0.3183	-25.70	-27.16	-28.9

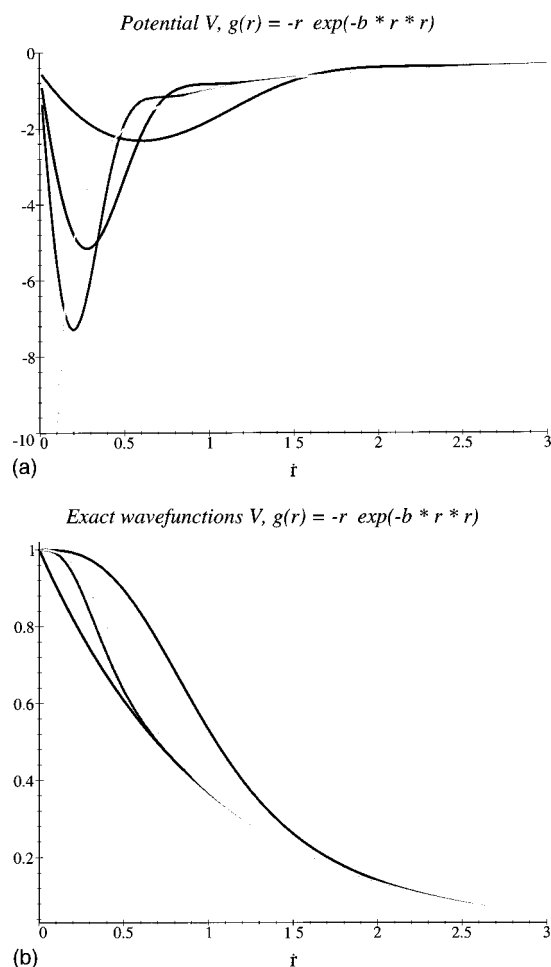


FIG. 3. (a) Potential  $V$ , generated by  $g(r) = -r e^{-br^2}$ . Included is the Coulomb potential  $-1/r$  and, in order of increasing closeness to  $-1/r$ ,  $V_V(r;b)$  for  $b = 1.0$ ,  $b = 5.0$ , and  $b = 10.0$ . (b) Corresponding exact radial wave functions for same values of  $b$ , in addition to  $e^{-r}$ .

#### IV. SURVEY OF POSSIBILITIES AND POTENTIAL PROBLEMS

At first sight, the range of possibilities for using transformations of the kind discussed in this paper appears to be quite extensive, and at least is food for thought. A key element is that the transformations apply to the coordinate representation of the Hamiltonian. Hence every theoretical model can potentially benefit from the improved numerical stability of the resulting eigenvalue equation. In this broad context, we can think, for example, of diffusion Monte-Carlo calculations, but also of DFT approaches that might be based on a transformed Hamiltonian. The treatment of the nuclear-electron cusp is similar in density-based and wave function-based approaches, while an important part of the electron correlation might be included automatically, starting from the transformed interactions. Similarly, Hartree-Fock or multiconfiguration self-consistent field (MCSCF) calculations based on the transformed Hamiltonian may already include the majority of the traditional correlation corrections. Self-consistent-field approaches will have to be based on a non-Hermitian Hamiltonian. In the realm of electron scattering, for example, such calculations have been carried out using complex scaling techniques.<sup>26</sup>

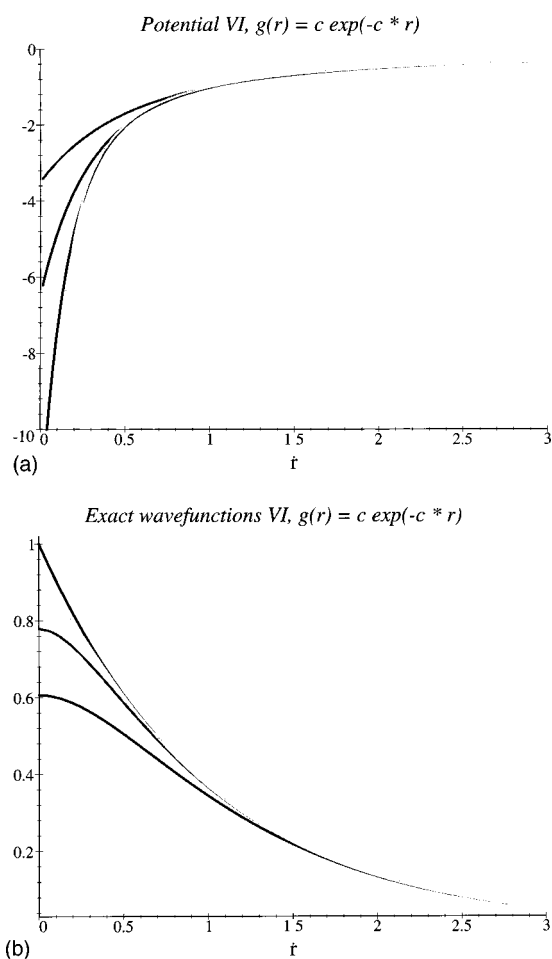


FIG. 4. (a) Potential  $VI$ , generated by  $g(r) = -(1/c)e^{-cr}$ . Included is the Coulomb potential  $-1/r$  and, in order of increasing closeness to  $-1/r$ ,  $V_{VI}(r;c)$  for  $c = 2.0$ ,  $c = 4.0$ , and  $c = 8.0$ . (b) Corresponding exact radial wave functions for same values of  $c$ , in addition to  $e^{-r}$ .

We note that as a consequence of the non-Hermiticity of the Hamiltonian, the density matrix is not symmetric either.

Another important area that might benefit is the calculation of properties, in particular properties like nuclear magnetic resonance (NMR) spin-spin coupling constants and zero-field splittings in electron spin resonance (ESR) spectroscopy, which depend on the value of the wave function at the nucleus.<sup>25,42</sup> The explicit treatment of the nuclear-electron cusp may be an essential simplification. However, our initial investigations for the hydrogen atom give mixed results and warrant caution. The fact that the cusp problem for the transformed left-hand wave function actually deteriorates is reason for concern. It indicates one might want to use different basis sets for the expansion of the ket state and the bra, or the projection manifold. As illustrated from the application to hydrogen in a finite basis set, the energy eigenvalue of the transformed Hamiltonian no longer presents an upper bound. This makes it difficult to gauge the accuracy of results. On the other hand, it may provide a means to systematically improve the energy coming from below.

The most immediate candidate for treatment is, of course, the electron-electron cusp. Our hope is that with the current approach we can reduce the basis set problem in  $ab$

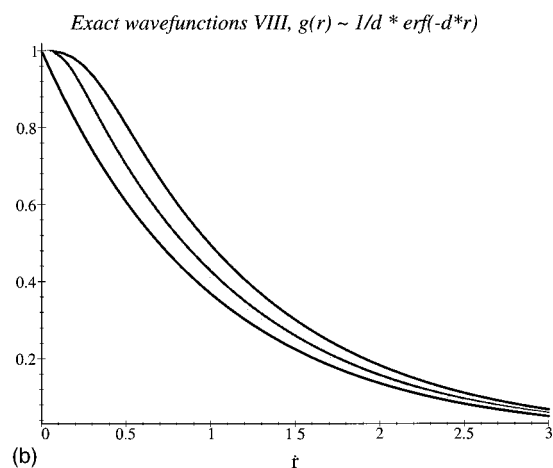
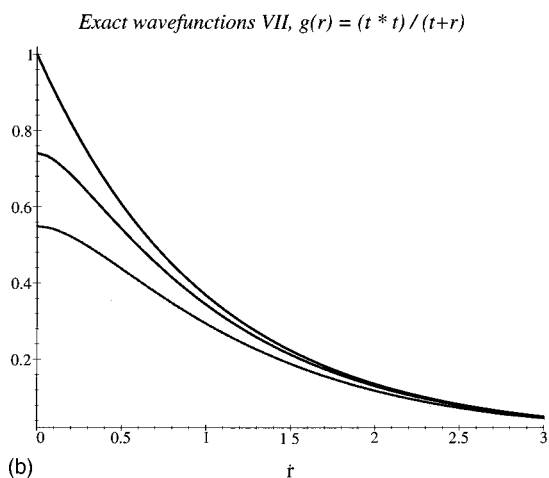
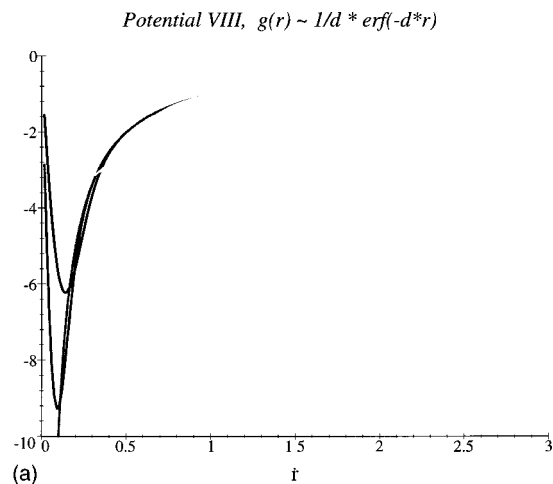
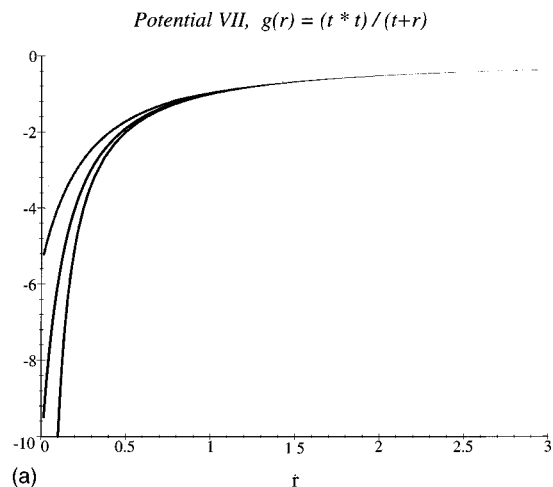


FIG. 5. (a) Potential VII, generated by  $g(r) = -t^2/(t+r)$ . Included is the Coulomb potential  $-1/r$  and, in order of increasing closeness to  $-1/r$ ,  $V_{VII}(r;t)$  for  $t=0.9$ ,  $t=0.6$ , and  $t=0.3$ . (b) Corresponding exact radial wave functions for same values of  $t$ , in addition to  $e^{-r}$ .

FIG. 6. (a) Potential VIII, generated by  $g(r) = -(\sqrt{\pi}/2d)\text{erf}(-dr)$ . Included is the Coulomb potential  $-1/r$  and, in order of increasing closeness to  $-1/r$ ,  $V_{VIII}(r;d)$  for  $d=3.0$ ,  $d=6.0$ , and  $d=9.0$ . (b) Corresponding exact radial wave functions for same values of  $t$ , in addition to  $e^{-r}$ .

*initio* electronic structure calculations, such that with rather modest basis sets like double zeta polarization (DZP) or triple zeta double polarization (TZ2P) one can achieve high accuracy. In the CCR12 method,<sup>23,36</sup> one overcomes the problem of the need for high angular momentum functions, but there is the unfortunate requirement of near completeness in the  $s$ ,  $p$  basis. A slight non-Hermiticity of the Hamiltonian should not cause major problems, and they can be dealt with straightforwardly in CC theory, which is nonsymmetric anyway. We note that there is certainly no upper bound on the total energies making it essential to look at observable quantities like excitation energies, dissociation energies, vibrational frequencies, densities etc. The most daunting problem is the occurrence of three-particle terms in the Hamiltonian. By choosing a suitable transformation, the range of the three-particle interaction can be made to be quite short, and this will be reflected by the sparsity of the three-particle integrals in the atomic basis set. However this sparsity will be lost if the integrals would be transformed to the molecular orbital (MO) basis. One can hope that inclusion of the three-particle interactions can be dealt with at the Hartree-Fock level. After the self-consistent field (SCF) calculation, the three-body

component of the Hamiltonian is written in normal order, yielding zero-particle, one-particle, two-particle, and finally three-particle operators. We would propose including up to two-particle components, while the three-body pure excitation operators might be taken together with a parenthesis  $T$  approximation on top of a CCSD calculation (for an overview of perturbative corrections to CCSD see Ref. 43, for example). The technical problem is choosing a suitable transformation that allows one to calculate the relevant integrals analytically and conveniently.

Finally, the reader might wonder if the transformations discussed in this paper might be applied to eliminate the long-range tail of the Coulomb potential. If we examine the form of the transformed two-electron interaction [Eq. (24)], this seems to require that  $\lim_{r \rightarrow \infty} g'(r) = 1$ . This, however, leads to an infinite range for the three-particle terms and the velocity-dependent interactions. Another possibility is that  $\lim_{r \rightarrow \infty} g''(r) \rightarrow (2q_i q_j \mu_{ij}/r)$ . This implies that  $g'(r)$  asymptotically tends to  $\ln(r)$ , an even more disastrous behavior. Therefore, we do not think the transformation can be used to simplify matters in the long-range regime.

In conclusion, the principal result of this paper is the

idea that an effective potential, based upon a similarity transformation of the Hamiltonian, can be developed to eliminate the cusp behavior in the normal Hamiltonian. The hope is that if a better behaved operator could be introduced that is easier to describe in a normal one-particle quantum chemical basis set, then the basis set error in quantum chemistry could be significantly reduced.

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