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Correcting Models with Long-Range Electron Interaction Using Generalized Cusp Conditions

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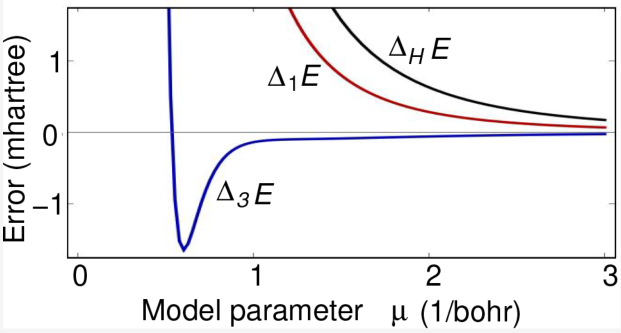
ABSTRACT: Sources of energy errors resulting from the replacement of the physical Coulomb interaction by its long-range erfc(μr)/r approximation are explored. It is demonstrated that the results can be dramatically improved and the range of μ giving energies within chemical accuracy limits significantly extended if the generalized cusp conditions are used to represent the wave function at small r. The numerical results for two-electron harmonium are presented and discussed.



■ THE PROBLEM TO BE SOLVED

We have a model system, $H(\mathbf{R};\ \mu)$, and a corresponding Schrödinger equation,

$$H(\mathbf{R};\ \mu)\Psi(\mathbf{R},\ \boldsymbol{\sigma};\ \mu) = E(\mu)\Psi(\mathbf{R},\ \boldsymbol{\sigma};\ \mu) \tag{1}$$

The system is composed of N electrons confined by an external potential, $\mathbf{R}$ and $\boldsymbol{\sigma}$ stand, respectively, for their orbital and spin coordinates. All quantities characterizing the system (e.g., energy or wave function) depend on the external potential, but we show this dependence explicitly only when the form of this potential is specified (e.g., the dependence on ω in the section "The Model System".

The interaction between electrons is described by a μ-dependent model potential $v_{\mathrm{int}}(r;\ \mu)$:

- $\mu = 0$: there is no interaction between electrons, so $v_{\mathrm{int}}(r;\ 0) = 0$.
- $\mu = \infty$: we have the physical, Coulomb interaction, so $v_{\mathrm{int}}(r;\ \infty) = 1/r$.
- $\mu \in (0,\ \infty)$: we choose

  $$v_{\mathrm{int}}(r;\ \mu) = w(r;\ \mu) = \frac{\mathrm{erf}(\mu r)}{r} \tag{2}$$

  where $r = r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$. Exploring other forms of interaction may be both interesting and useful as, for example, in ref 1.

To simplify the notation, we drop μ when $\mu = \infty$.

We assume that the solutions of eq 1 are accessible for selected finite values of μ. However, we are not interested in the model system energy, $E(\mu)$. We aim at determining E corresponding to the physical interaction. Stated differently, we are interested in

$$\bar{E}(\mu) = E - E(\mu) \equiv -\Delta_0 E(\mu) \tag{3}$$

where $\Delta_0 E(\mu)$ is referred to as the *error of the energy of the model system*.

To get an idea about the change of $\bar{E}(\mu)$ with respect to μ, we show in Figure 1 some situations where E is known for arbitrary precision. By construction, $\bar{E}(\infty) = 0$. As μ decreases, the interaction weakens and disappears for $\mu = 0$. This effect, not compensated by any change in the external potential, leads to the absolute values of $\bar{E}(\mu)$ increasing with decreasing μ and becoming very large for sufficiently small μ.

In this paper we explore how much one can lower the values of μ and, by correcting the model, still retain approximations of $\bar{E}$ within the chemical accuracy (±1 kcal/mol) error bars.

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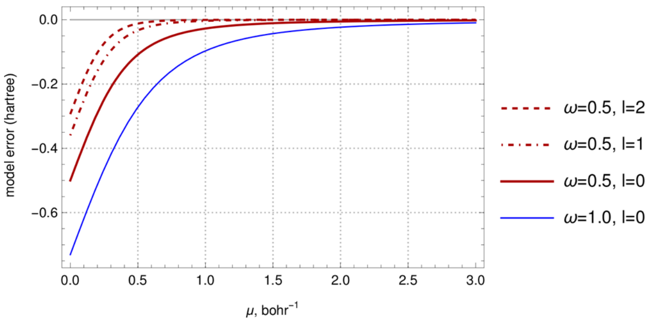

Figure 1. Error of the energy of the model system, $\Delta_0 E(\mu)$, for the lowest energy state of harmonium with $\omega = 1/2$ (red curves) and $\omega = 1$ (thin blue curve), for $l = 0$, full curves; $l = 1$, dot-dashed curve; $l = 2$, dashed curve.

CORRECTING MODELS

Energy Extrapolation—A Historic Solution. A way proposed in ref [2] is to expand $\overline{E}(\mu)$ in the following basis,

$$\overline{E}(\mu) \approx \sum_{k=1}^{M} \overline{e}_k \chi_k(\mu) \tag{4}$$

Here $\chi_k(\mu)$, $k = 1, ..., M$ are some basis functions, and $\overline{e}_k$ are coefficients to be determined. There are different ways to determine these coefficients once the basis functions are given. One option is to obtain them from the derivatives of $E(\mu)$ with respect to μ. This corresponds to (generalized) Taylor expansions or to perturbation theory. Another possibility is calculating $E(\mu)$ for several values of μ and then matching the results to the expansion. This method is called energy extrapolation:[2] from model information, we aim to reach the physical result.

One way to achieve our aim is to introduce more parameters into the Hamiltonian,[3] e.g.,

$$H(\mathbf{R};\lambda,\mu) = H(\mathbf{R};\mu) + \lambda[H(\mathbf{R}) - H(\mathbf{R};\mu)] \tag{5}$$

The eigenvalue and the corresponding eigenfunction of $H(\mathbf{R};\lambda,\mu)$ are, respectively, $E(\lambda,\mu)$ and $\Psi(\mathbf{R},\boldsymbol{\sigma};\lambda,\mu)$; notice that $E(\mu) = E(\lambda,\mu)|_{\lambda=0}$. In the Hamiltonian (eq 5), the interaction potential is

$$v_{\text{int}}(r;\lambda,\mu) = w(r;\mu) + \lambda\overline{w}(r;\mu)$$

where

$$\overline{w}(r;\mu) = \frac{1}{r} - w(r;\mu) = \frac{1-\text{erf}(\mu r)}{r} = \frac{\text{erfc}(\mu r)}{r} \tag{6}$$

Therefore,

$$v_{\text{int}}(r;\lambda,\mu) = (1-\lambda)\frac{\text{erf}(\mu r)}{r} + \frac{\lambda}{r} \tag{7}$$

We see that we can reach the physical result either with $\lambda = 1$ or with $\mu = \infty$. "Shooting" from different points to the same target may simplify our task. However, this is not further discussed in this paper.

Energy extrapolation has an important problem: we do not know how to choose $\chi_k(\mu)$. What makes the problem worse is that we are not willing to use many basis functions. Ideally, we should use a single function, that is to perform a single model calculation, $M = 1$ in eq 4.

The Adiabatic Connection. For $\|\Psi(\mathbf{R},\boldsymbol{\sigma};\lambda,\mu)\| = 1$ the Hellmann−Feynman theorem yields

$$\partial_\lambda E(\lambda,\mu) = \langle\Psi(\mathbf{R},\boldsymbol{\sigma};\lambda,\mu)|\partial_\lambda H(\mathbf{R};\lambda,\mu)|\Psi(\mathbf{R},\boldsymbol{\sigma};\lambda,\mu)\rangle = \langle\overline{w}(\lambda,\mu)\rangle \tag{8}$$

where

$$\langle\overline{w}(\lambda,\mu)\rangle = \langle\Psi(\mathbf{R},\boldsymbol{\sigma};\lambda,\mu)|\overline{W}(\mathbf{R};\mu)|\Psi(\mathbf{R},\boldsymbol{\sigma};\lambda,\mu)\rangle \tag{9}$$

and

$$\overline{W}(\mathbf{R};\mu) \equiv H(\mathbf{R}) - H(\mathbf{R};\mu) = \sum_{1\le i<j\le N}\overline{w}(r_{ij};\mu) \tag{10}$$

By integrating eq 8 over λ, one obtains

$$\overline{E}(\mu) = \int_0^1 \langle\overline{w}(\lambda,\mu)\rangle\, \mathrm{d}\lambda \tag{11}$$

(Notice that E could have also been obtained by integration over μ, as $E = E(1,\mu) = E(\lambda,\infty)$.) The integrand in eq 11, an integral over $3N$-dimensional configuration space and 2^N-dimensional spin space, can be reduced to a one-dimensional radial integral. Exploiting the antisymmetry of the wave function and integrating over spin and over coordinates of electrons 3, 4, ..., N, yields[4]

$$\langle\overline{w}(\lambda,\mu)\rangle = \int_{\mathbb{R}^6}\overline{w}(r_{12};\mu)\Gamma_{\lambda,\mu}(\mathbf{r}_1,\mathbf{r}_2)\, \mathrm{d}\mathbf{r}_1\, \mathrm{d}\mathbf{r}_2 \tag{12}$$

where

$$\Gamma_{\lambda,\mu}(\mathbf{r}_1,\mathbf{r}_2) = \binom{N}{2}\sum_{\sigma_1,\ldots,\sigma_N}\int_{\mathbb{R}^{3N-6}}|\Psi(\mathbf{R},\boldsymbol{\sigma};\lambda,\mu)|^2\, \mathrm{d}\mathbf{r}_3\, \mathrm{d}\mathbf{r}_4\cdots \mathrm{d}\mathbf{r}_N$$

is the diagonal part of the second-order reduced density matrix, 2RDM, corresponding to $\Psi(\mathbf{R},\boldsymbol{\sigma};\lambda,\mu)$; the sum is extended over spin coordinates of all electrons.

After introducing the relative-motion variables

$$\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2,\ \mathbf{r}^+ = \frac{\mathbf{r}_1 + \mathbf{r}_2}{2} \tag{13}$$

performing integration over $\mathbf{r}^+$ and expressing $\mathbf{r}$ in spherical coordinates, $\mathbf{r}(r,\theta,\phi)$, eq 12 can be rewritten as

$$\langle\overline{w}(\lambda,\mu)\rangle = \int_{\mathbb{R}^6}\overline{w}(r;\mu)\Gamma_{\lambda,\mu}(\mathbf{r},\mathbf{r}^+)\, \mathrm{d}\mathbf{r}\, \mathrm{d}\mathbf{r}^+ = \int_{\mathbb{R}^3}\overline{w}(r;\mu)\gamma(\mathbf{r};\lambda,\mu)\, \mathrm{d}\mathbf{r} \tag{14}$$

where $\mathrm{d}\mathbf{r} = r^2\, \mathrm{d}r \sin\theta\, \mathrm{d}\theta\, \mathrm{d}\phi$, $r = r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$, and $\gamma(\mathbf{r};\boldsymbol{\lambda},\mu)$ is the diagonal part of the first-order reduced density matrix, 1RDM. Since in the coordinate space $\overline{w}(r;\mu)$ depends on the radial coordinate r only, we can do the spherical averaging. In effect, the integrand of eq 11 is simplified to

$$\langle\overline{w}(\lambda,\mu)\rangle = \int_0^\infty \overline{w}(r;\mu)\tilde{\gamma}(r;\lambda,\mu)r^2\, \mathrm{d}r \tag{15}$$

where

$$\tilde{\gamma}(r;\lambda,\mu) = \int_0^{2\pi}\int_0^{\pi}\gamma(\mathbf{r};\lambda,\mu)\sin\theta\, \mathrm{d}\theta\, \mathrm{d}\phi$$

The adiabatic connection defined in eq 11 carries no practical information, as it requires the knowledge of $\langle\overline{w}(\lambda,\mu)\rangle$ for all values of λ, while in the present approach it is known only for $\lambda = 0$.

At the limit of $r \to 0$, $\overline{w}(r;\mu) \sim 1/r$. Therefore, also for large μ, $\overline{w}(r;\mu)$ is non-negligible if r is small enough. As is shown hereafter, the information necessary for correcting the model at small r can be derived from the generalized cusp conditions (GCC).

Generalized Cusp Conditions. The information about the behavior of the wave function in the vicinity of the coalescence point, i.e., for $r = r_{12} \ll 1$, can be derived from general properties of the Schrödinger equation at $r \to 0$. In general, the approach is based on the expansion of the wave function and of the potential as the power series of r and deriving conditions that have to be fulfilled by the expansion coefficients in order to retain the consistency of the Hamiltonian eigenvalue problem. The simplest and most commonly known is the Kato's cusp condition,[5] which can be derived from the requirement that in the case of the electrostatic interaction the local energy at $r = 0$ is nonsingular. Higher order (generalized) cusp conditions can be obtained from the demand that the local energies generated by powers of the Hamiltonian are nonsingular (energy-independent conditions) and ratios of the local energies generated by the consecutive powers are constant (energy-dependent conditions).[6] Alternatively, one can use the expansion of the wave function in powers of r and require that the Schrödinger equation is statisfied.[7−9] Both approaches are equivalent, but the conditions derived from the former one, though more complicated, have more transparent physical meaning.

In this paper the GCCs are applied to describe the r-dependence of the wave function in the area of small r, where the model interaction potential departs from the physical one.

THE MODEL SYSTEM

The simplest nontrivial model system containing one pair of electrons is composed of three particles: two electrons interacting by a repulsive model potential, and a third particle, "nucleus", which interacts with electrons by an attractive force. Commonly known examples of such systems are helium atom, the nucleus attracts electrons by the Coulomb force, and harmonium (Hooke atom), the nucleus attracts electrons by the Hooke force. After the separation of the center of mass, the system is reduced to two interacting particles in an external potential v_{ext}. In the case of harmonium,

$$v_{\text{ext}}(r_1, r_2; \omega) = \frac{\omega^2}{2}(r_1^2 + r_2^2) \tag{16}$$

The potential depends on a parameter, ω, which defines the strength of the confinement. In the case of quantities that depend on this potential, the dependence on ω is explicitly shown. For example, $E(\omega, \mu)$ stands for the special case of $E(\mu)$, corresponding to the external potential (eq 16).

To our knowledge, harmonium is the only bound system containing a pair of interacting electrons for which the Schrödinger equation is known to be separable. Apart from the three-dimensional free-particle equation describing the motion of the center of mass, the two-particle Schrödinger equation for harmonium is separable into six one-dimensional equations: five are exactly solvable, and the sixth one can be solved numerically to an arbitrary precision (for some specific values of ω it is also solvable analytically). It is important to note that the separability holds for all forms of the interaction potential including the form given by $v_{\text{int}}(r; \lambda, \mu)$. (In principle, the term "harmonium" refers to two confined Coulomb-interacting electrons. In this paper, we extend this term to the case of model potentials v_{int}.) Therefore, harmonium is particularly suitable for pilot studies of the consequences of using various non-Coulombic forms of the interaction potentials. Motivated by these observations, at this stage, we explore our problem using harmonium as the model system.

The Schrödinger equation for harmonium

$$[T(\mathbf{r}_1, \mathbf{r}_2) + v_{\text{ext}}(r_1, r_2; \omega) + v_{\text{int}}(r; \lambda, \mu) - \mathcal{E}(\rho)]\Psi(\mathbf{r}_1, \mathbf{r}_2; \rho) = 0 \tag{17}$$

where $T(\mathbf{r}_1, \mathbf{r}_2)$ is two-particle kinetic energy operator, depends on three parameters, collectively denoted $\rho = \{\omega, \lambda, \mu\}$, and $\Psi(\mathbf{r}_1, \mathbf{r}_2; \rho)$ is the orbital part of the two-electron wave function. After transformation (eq 13), eq 17 can by split into two spherically symmetric equations. The first one depends on the interaction potential and describes the relative motion of electrons:

$$[-\Delta_{\mathbf{r}} + v(r; \rho) - E(\rho)]\psi_{\text{rel}}(\mathbf{r}; \rho) = 0 \tag{18}$$

where

$$v(r; \rho) = \frac{\omega^2 r^2}{4} + v_{\text{int}}(r; \lambda, \mu) = \frac{\omega^2 r^2}{4} + (1 - \lambda)\frac{\operatorname{erf}(\mu r)}{r} + \frac{\lambda}{r} \tag{19}$$

The second equation describes the motion of the center of mass of the electron pair in the external potential:

$$\left[-\frac{\Delta_{\mathbf{r}^+}}{4} + \omega^2(r^+)^2 - \mathrm{E}(\omega)\right]\psi_{\text{cm}}(\mathbf{r}^+; \omega) = 0 \tag{20}$$

where $r^+ = |\mathbf{r}^+|$. By construction, we have

$$\mathcal{E}(\rho) = E(\rho) + \mathrm{E}(\omega), \quad \Psi(\mathbf{r}_1, \mathbf{r}_2; \rho) = \psi_{\text{rel}}(\mathbf{r}; \rho)\psi_{\text{cm}}(\mathbf{r}^+; \omega) \tag{21}$$

The interaction potential appears only in eq 18. So, for our study, we deal with this equation only. The potential is spherically symmetric. Therefore,

$$\psi_{\text{rel}}(\mathbf{r}; \rho) = \psi_l(r; \rho)Y_{lm}(\theta, \phi) \tag{22}$$

where $\psi_l(r; \rho)$ is determined by the radial equation

$$\left[-\frac{\mathrm{d}^2}{\mathrm{d}r^2} + \frac{l(l+1)}{r^2} + v(r; \rho) - E(\rho)\right][r\psi_l(r; \rho)] = 0 \tag{23}$$

The two-electron wave function, $\Psi(\mathbf{r}_1, \mathbf{r}_2; \rho)$, symmetric/antisymmetric with respect to the transposition of $(\mathbf{r}_1, \mathbf{r}_2)$ correspond to singlet/triplet. As one can see, singlet states correspond to the even parity (even l) spherical harmonics in eq 22, and triplet states to the odd ones.

Generalized Cusp Conditions for the Model System. Using[10]

$$\frac{\operatorname{erf}(\mu r)}{r} = \frac{2\mu}{\sqrt{\pi}}\left(1 - \frac{(\mu r)^2}{3 \cdot 1!} + \frac{(\mu r)^4}{5 \cdot 2!} - \frac{(\mu r)^6}{7 \cdot 3!} + \ldots\right)$$

one can expand the potential (eq 19) as

$$v(r; \rho) = \sum_{i=-1}^{\infty} v_i(\rho)r^i \tag{24}$$

with

$$v_{-1} = \lambda, \quad v_0 = (1 - \lambda)\frac{2\mu}{\sqrt{\pi}}, \quad v_1 = 0, \quad v_2 = \frac{\omega^2}{4} - (1 - \lambda)\frac{2\mu^3}{3\sqrt{\pi}},$$
$$v_3 = 0, \quad \ldots \tag{25}$$

The wave function, for small r, can be represented by the following power series

$$\psi_l(r; \rho) \approx r^l \sum_{k=0}^{K} c_k(\rho)r^k = c_0(\rho)r^l \sum_{k=0}^{K} \tilde{c}_k(\rho)r^k \tag{26}$$

where $\tilde{c}_k(\rho) = c_k(\rho)/c_0(\rho)$. General formulas for GCC are given in refs 6−9. Here we give equations defining $\tilde{c}_k$ for $k \leq 4$:

$$\begin{gathered}
A_1\widetilde{c_1} + \nu_{-1} = 0,\\
A_2\widetilde{c_2} + \nu_{-1}\widetilde{c_1} - \epsilon = 0,\\
A_1A_3\widetilde{c_3} + (A_1 + A_2)\nu_{-1}\widetilde{c_2} + \nu_{-1}^2\widetilde{c_1} + A_1\nu_1 = 0,\\
A_2A_4\widetilde{c_4} + (A_2 + A_3)\nu_{-1}\widetilde{c_3} + \nu_{-1}^2\widetilde{c_2} + A_2\nu_1\widetilde{c_1} + (\nu_{-1}\nu_1 + A_2\nu_2 - \epsilon^2) = 0,\\
\dots\dots\dots
\end{gathered} \tag{27}$$

where $A_i = -i(2l + i + 1)$ and $\epsilon = E - \nu_0$. Coefficients $\tilde{c}_k$, energy parameter ϵ, and coefficients ν_i depend on the parameters ω, λ, and μ. For simplicity, in eq 27 this dependence has not been shown explicitly. All coefficients $\tilde{c}_k$ depend on l and on ν_{-1}. The coefficients $\tilde{c}_k$, with $k \geq 3$, depend on ν_1. In general, ν_i shows up in $\tilde{c}_k$, with $k \geq (i + 2)$.[6] The external potential is proportional to r^2 and vanishes at $r = 0$. Therefore, in expansion (eq 26) the ω dependence begins at $\tilde{c}_4$.

For the construction of $\tilde{c}_k$ with even values of k, the state energy is needed. In these cases we use the expectation value of the Hamiltonian defined in eq 5:

$$E(\omega, \lambda, \mu) \approx E(\omega, \mu) + \lambda\langle\overline{w}(r; \omega, 0, \mu)\rangle$$

where $E(\omega, \mu) = E(\omega, \lambda, \mu)\,|_{\lambda=0}$. For the definition of $\langle\overline{w}(r; \omega, \lambda, \mu)\rangle$, see eq 28. Numerical tests using the exact $E(\omega, \lambda, \mu)$ have shown that this approximation is negligible in comparison to the other approximations made in the present paper.

Dependence on λ and Normalization. The GCC provides only ratios $c_k(\rho)/c_0(\rho) \equiv \tilde{c}_k(\rho)$. If $\psi_l(r; \rho)$ is known in the whole range of r then $c_0(\rho)$ can be determined by the normalization condition. In our case this approach is non-applicable since only the small-r part of $\psi_l(r; \rho)$ is defined by the cusp conditions. But $c_0(\rho)$ appears as a prefactor in the approximation (eq 26) for $\psi_l(r; \rho)$, and its value is necessary for any practical use of this approximation. Therefore, $c_0(\rho)$ has to be estimated in a different way using only the information about the short-range behavior of the wave function.

We have to introduce additional information to deal with this issue. Let us first consider the dependence of c_0 on λ. It is needed for the adiabatic connection expression (eqs 11 and 15). We select $||\psi_{\mathrm{cm}}(\mathbf{r}^+; \omega)|| = 1$. Then the substitution of the wave function defined in eqs 21 and 22, and of its expansion (eq 26), to eq 14 yields

$$\begin{aligned}
\langle\overline{w}(\rho)\rangle &= \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} |\psi_{\mathrm{rel}}(\mathbf{r}; \rho)|^2\overline{w}(r; \mu)r^2 \;\mathrm{d}r\; \sin\theta\; \mathrm{d}\theta\; \mathrm{d}\phi\\
&= \int_0^{\infty} |\psi_l(r; \rho)|^2\overline{w}(r; \mu)r^2 \;\mathrm{d}r,\\
&\approx |c_0(\rho)|^2 \int_0^{\infty} \left| r^{l+1}\sum_{k=0}^{K} \tilde{c}_k(\rho)r^k \right|^2 \overline{w}(r; \mu)\; \mathrm{d}r
\end{aligned} \tag{28}$$

and according to eq 11,

$$\overline{E}(\omega, \mu) = \int_0^1 \langle\overline{w}(\omega, \lambda, \mu)\rangle\; \mathrm{d}\lambda \tag{29}$$

For models close to the exact interaction (for large μ), one can derive the following relationship[3,11] (a derivation is given in the Appendix):

$$c_0(\omega, \lambda, \mu) \underset{\mu\to\infty}{\sim} \mathcal{N}\left(1 + \frac{1 - \lambda}{\sqrt{\pi}\mu} + O(\mu^{-2})\right) \tag{30}$$

where $\mathcal{N}$ is a still unknown normalization constant. As one can see,

$$\mathcal{N} = c_0(\omega, 1, \mu) = c_0(\omega, \lambda, \infty) \equiv c_0(\omega)$$

Notice that $c_0(\omega, 1, \mu)$ and $c_0(\omega, \lambda, \infty)$ do not depend, respectively, on μ and λ and are equal to $c_0(\omega)$ corresponding to the physical (Coulomb) interaction potential.

We introduce the notation

$$\mathcal{I}_K(\omega, \lambda, \mu) = \left(1 + \frac{1 - \lambda}{\sqrt{\pi}\mu}\right)^2 \int_0^{\infty} \left[r^{l+1}\sum_{k=0}^{K} \tilde{c}_k(\omega, \lambda, \mu)r^k\right]^2 \overline{w}(r, \mu)\; \mathrm{d}r \tag{31}$$

As stated at the beginning of this Article, we know the model wave function at $\lambda = 0$. Therefore, we can calculate

$$\langle\overline{w}(\omega, 0, \mu)\rangle = \int_0^{\infty} |\psi(r, \omega, 0, \mu)|^2\overline{w}(r, \mu)r^2\; \mathrm{d}r \tag{32}$$

Since $\mathcal{N}$ does not depend on λ, we can assume that

$$\mathcal{N}^2 \approx \frac{\langle\overline{w}(\omega, 0, \mu)\rangle}{\mathcal{I}_K(\omega, 0, \mu)} \tag{33}$$

Combining eqs 29, 28, and 33, we get

$$\overline{E}(\omega, \mu) \approx \frac{\langle\overline{w}(\omega, 0, \mu)\rangle}{\mathcal{I}_K(\omega, 0, \mu)} \int_0^1 \mathcal{I}(\omega, \lambda, \mu)\; \mathrm{d}\lambda \tag{34}$$

Corrections to the Model. Assume that ω is fixed and $\lambda = 0$. For simplicity, in the next equations, we skip these parameters. Also the r-dependence, in most cases obvious, is not shown explicitly. We designate μ-dependence only, retaining the convention that we drop μ, if $\mu = \infty$. Our model is defined by the analog of eq 1:

$$H(\mu)\psi(\mu) = E(\mu)\psi(\mu), \quad \text{i.e.,} \quad E(\mu) = \langle\psi(\mu)|H(\mu)|\psi(\mu)\rangle \tag{35}$$

For the physical (Coulombic) interaction, $\mu = \infty$ and we have $E = \langle\psi|H|\psi\rangle$.

As we already said, the solutions of the crude model, $E(\mu)$ and $\psi(\mu)$, are known. The error of this model, $\Delta_0E(\mu)$, has been defined in eq 3. Our aim is to add corrections to the model. The first-order perturbation correction to $E(\mu)$ is

$$\langle\psi(\mu)|H - H(\mu)|\psi(\mu)\rangle = \langle\psi(\mu)|\overline{w}(\mu)|\psi(\mu)\rangle \tag{36}$$

From here we have the correction:

$$\Delta_{\mathrm{H}}E(\mu) = \langle\psi(\mu)|H|\psi(\mu)\rangle - E = E(\mu) - E + \langle\overline{w}(\mu)\rangle \tag{37}$$

Plots of $\Delta_0E(\mu)$ and $\Delta_{\mathrm{H}}E(\mu)$ are given in Figure 2. At $\mu = 0$, that is, for the noninteracting system, $\Delta_0E(\mu)$ is huge. For the ground state of harmonium with $\omega = 1/2$, $E(\mu = 0) = 0.75$ instead of $E = 1.25$ hartree, giving $\Delta_0E(\mu) = 0.5$ hartree. But, $\Delta_0E(\mu)$ does not fall to the chemical accuracy error bars in the entire range of μ − up to 3 bohr^{-1}. The improvement due to the first-order perturbation (without any reference to a specific structure of the wave function) is impressive. For $\Delta_{\mathrm{H}}E(\mu)$, the chemical accuracy is reached if $\mu > 1.5$ bohr^{-1}. The error at $\mu = 0$ is reduced from 0.5 hartree to ∼0.06 hartree, that is of the same order of magnitude as obtained with mean-field approximations (∼0.04 hartree for Hartree−Fock or Kohn−Sham). The sign of the errors in Figure 2 is (i) negative for $E(\mu) - E$ (as $w(r, \mu) \leq 1/r$) and (ii) positive for $\langle\psi(\mu)|H|\psi(\mu)\rangle - E$ (by the variational principle).

Equation 34 may be rewritten as

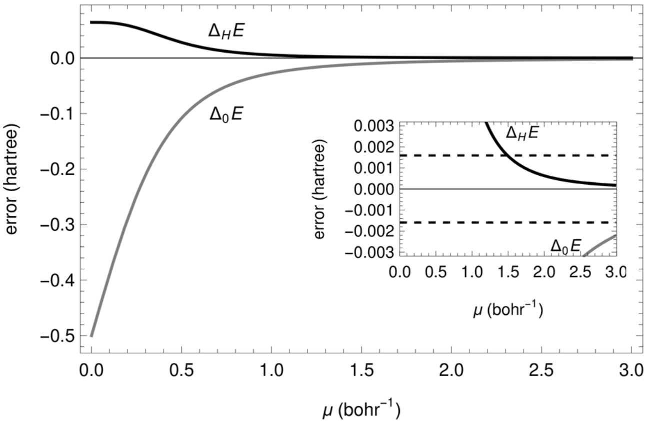

Figure 2. Errors of the model energy, $\Delta_0 E(\mu)$, eq 3, gray curve, and of the expectation value of the physical Hamiltonian, H, with the model wave function, $\psi(\mu)$, $\Delta_H E(\mu)$, eq 37, black curve, for the ground state of harmonium with $\omega = 0.5$. The inset zooms on the same curves (by 2 orders of magnitude), the horizontal dashed lines indicating the region of "chemical accuracy" (±1 kcal/mol).

$$\Delta_K E(\mu) = E(\mu) - E + C_{\mathcal{I}}^K \langle \overline{w}(\mu) \rangle \tag{38}$$

where

$$C_{\mathcal{I}}^K = \frac{1}{\mathcal{I}_K(\omega, 0, \mu)} \int_0^1 \mathcal{I}(\omega, \lambda, \mu)\, \mathrm{d}\lambda \tag{39}$$

Equation 38 can be interpreted as a generalization of eqs 3 and 37. The prefactor of $\langle \overline{w}(\mu) \rangle$ in these two equations is, respectively, 0 and 1. Prefactor $C_{\mathcal{I}}^K$ in eq 38 has been derived using some information about the structure of the wave function, specifically, GCC and the adiabatic connection. Therefore, one can expect that

$$|\Delta_0 E(\mu)| \gg |\Delta_\mathrm{H} E(\mu)| \gg |\Delta_\mathrm{K} E(\mu)| \tag{40}$$

The correctness of this expectation is demonstrated in the next section.

The integrals over r in eq 31 can be computed analytically[10]

$$\int_0^\infty \operatorname{erfc}(\mu r) r^k \, \mathrm{d}r = \frac{k\Gamma(k/2)}{2\sqrt{\pi}(k+1)\mu^{k+1}} \tag{41}$$

Therefore, $\mathcal{I}_K(\omega, \lambda, \mu)$ can be expressed as an algebric function of ω, λ, and μ. Explicit formulas for $\tilde{c}_k(\rho)$ can be easily deduced from eq 27. Consequently, the effort for computing the prefactor $C_{\mathcal{I}}^K$ in eq 38 is negligible. Notice that in eq 41 $\Gamma(k/2)$ introduces a fast increase to the absolute value of $\mathcal{I}_K(\omega, \lambda, \mu)$ with K (the maximum power of r in the expansion).

The approximation is valid only asymptotically for sufficiently large μ. Notice that expressions (eq 30) for $c_0(\rho)$ and $\mathcal{I}(\rho)$ given in eqs 30 and 31 are divergent at $\mu = 0$.

■ RESULTS

General Considerations. In the following we will consider only harmonium systems. Of course, this can be seen as futile, because solving the one-dimensional differential Schrödinger equation, eq 23, is trivial (to obtain accurate results, we did it on a grid of the order of 10^5 points). The choice of this simple system is motivated by the desire to study uniquely the effect of the approximations introduced without adding other effects, such as the dependence on the one-particle basis set or the expansion in terms of Slater determinants. To avoid introducing new effects, the one-particle (external) potential is independent of μ. In view of future practical applications, we are interested to see how weak the model interaction can be taken (how small μ can be chosen) and still obtain an estimate of the energy within "chemical accuracy".

We now define the "smallest acceptable μ", SAμ: for $\mu \geq$ SAμ, the absolute errors are smaller than the chemical accuracy (1 kcal/mol). The range of errors between ±1 kcal/mol is indicated in the plots by horizontal dashed lines. For the system considered in Figure 2, $E(\mu)$ has a SAμ slightly above 3 bohr^{-1}. So, it is not interesting to discuss corrections if the interaction already reaches this strength. Weaker interactions can be considered if we simply correct the energy to first order, with $\langle \psi(\mu) | H | \psi(\mu) \rangle$, SA$\mu \approx 1.5$.

In the following, the presented plots show the errors of the approximations of E as functions of μ using the same scale as the inset in Figure 2.

How Weak Can the Interaction Be? Let us consider the ground state of harmonium with $\omega = 1/2$. Now we use the GCC to correct the model energy, $E(\mu)$ as in eqs 34 and 38, and cut off the expansion of the wave function $\psi(r, \rho)$, limiting the expansion in eq 26 to a maximal power of r, $K = 1, 2, 3$, and 4, see Figure 3a. When $K = 1$ we satisfy only Kato's cusp condition. This improves over $E(\mu)$, and also over first-order perturbation theory, bringing the SAμ to 1.3 bohr^{-1}. Increasing K further reduces the SAμ until a "wall" at around 0.5 bohr^{-1} is reached. Notice that not only the error is reduced by increasing K, but also the stability with respect to the change of the results by chaning μ is increased when going beyond satisfying only the Kato cusp condition. This is important because (i) in practice, there is an arbitrariness in the choice of μ, and (ii) the SAμ is system-dependent, as will be illustrated further down. The latter is of importance for size-consistency.

The derivations presented above never supposed that the state considered corresponds to the ground state. So, let us now consider some excited states. We consider first the lowest energy states with $l = 1$ and 2. The first corresponds to a triplet state, (Figure 3b), the second to a non-natural singlet state[12] (Figure 3c); for $l = 2$, the singlet cusp condition does not give a prefactor $(1 + r/2)$, but $(1 + r/6)$. King[13] remarks that, in an orbital picture, the $l = 2$ state corresponds to a strong mixture of sd and p^2 configurations. Notice that both the values provided by the model and the expectation value of the physical Hamiltonian are now in much better agreement with the exact value than for $l = 0$: the prefactor r^l appearing in eq 26 already keeps the electrons apart. Even for $K = 4$, for this system and these states, there is no significant gain over using just $\langle \psi(\mu) | H | \psi(\mu) \rangle$. For $l = 2$, the SAμs obtained for $K \leq 4$ are not improved over that of the expectation value of the Hamiltonian.

We also present the first two excited states with $l = 0$, Figure 3d,e. The model system has much larger errors which fall outside the domain of the plots. We notice an overall worsening ot the quality of the approximations. The model shows errors that fall outside the range of the plots. The SAμ for the expectation value of the Hamiltonian is around 2 bohr^{-1}. Using the Kato cusp condition reduces it to ≈1.5 bohr^{-1}. Increasing the order of the expansion, K, moves the SAμ down to somewhere between 1 and 0.5 bohr^{-1}.

We have seen above that the SAμs can be quite sensitive to the state described. They can also be sensitive to the system. Modifying ω affects the SAμs. Figure 3f,g show the effect of

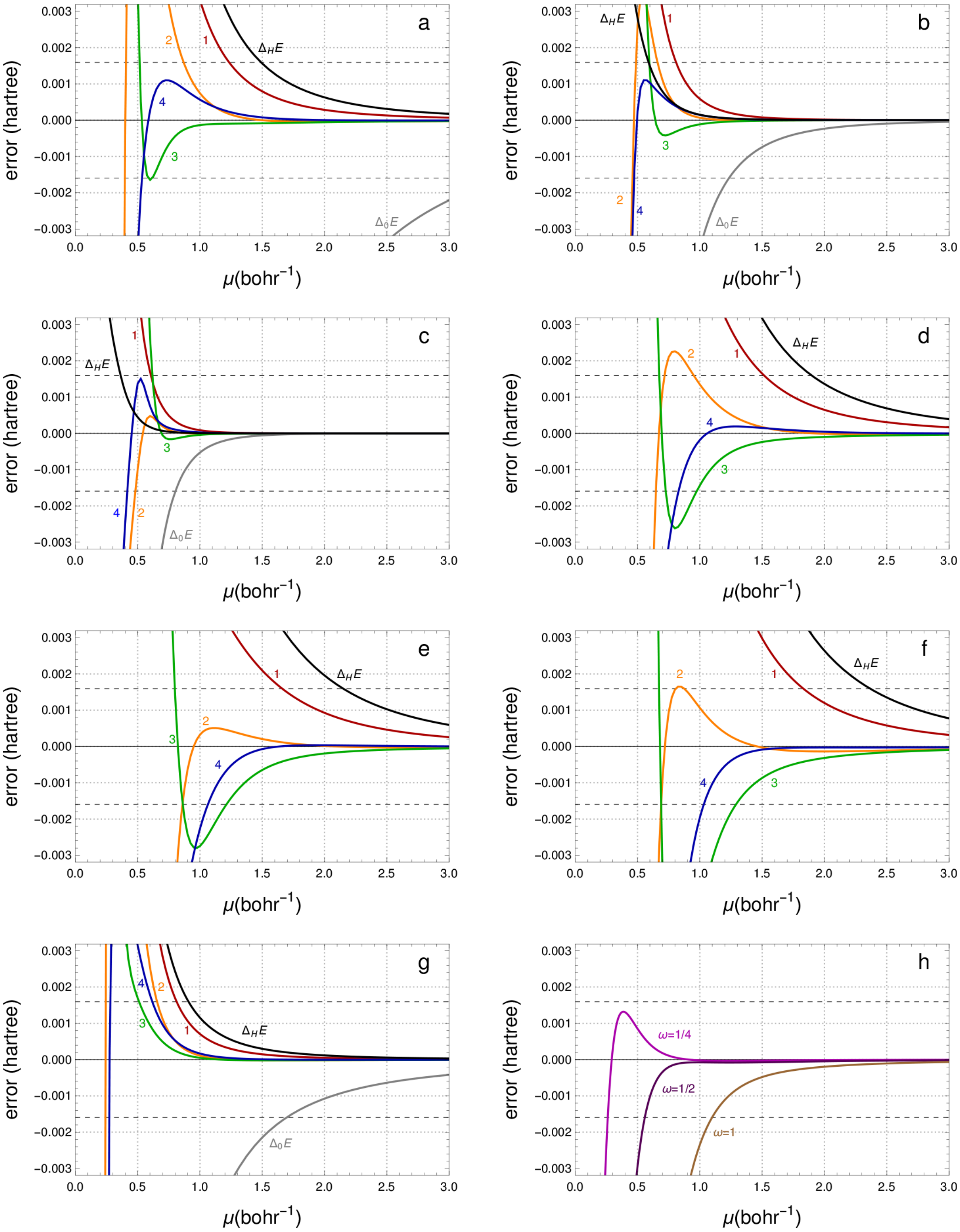

Figure 3. Errors of the different approximations for the energy of harmonium systems. The errors of the model energy, $\Delta_0 E(\mu)$, eq 3 are represented as gray curves, that of the expectation value of the physical Hamiltonian with the model wave function, $\Delta_{\mathrm{H}} E(\mu)$, eq 37, by black curves. Panels a−g show the errors for different orders K in the GCC expansion, eq 26, the value of K being indicated next to the curve. Panel h shows the error of the approximation of order μ^{-4}, as given in eq 42. Chemical accuracy (±1 kcal/mol) is indicated by horizontal dashed lines. a: $\omega = 1/2, n = 1, l = 0$; b: $\omega = 1/2, n = 1, l = 1$; c: $\omega = 1/2, n = 1, l = 2$; d: $\omega = 1/2, n = 2, l = 0$; e: $\omega = 1/2, n = 3, l = 0$; f: $\omega = 1, n = 1, l = 0$; g: $\omega = 1/4, n = 1, l = 0$; h: $\omega = 1/4$, 1/2, or 1, and $n = 1, l = 0$.

making the system more compact ($\omega = 1$ au) or diffuse ($\omega = 1/4$ au) for the respective ground states.

Comparisons. Using the GCC is not the only way to describe the short-range behavior. One can replace the expansion in powers of r, eq 26, by a simple form that does not diverge as $r \to \infty$. For example, one can ignore all terms arising from the external potential and the energy in the Schrödinger equation, in the limit $\mu \to \infty$, and we get, to order μ^{-4} (see ref 11 and eq 21 in ref 3),

$$\frac{\int_0^1 \mathrm{d}\lambda \mathcal{I}(\lambda, \mu)}{\mathcal{I}(\lambda = 0, \mu)} = \frac{\mu^2 + 1.06385\mu + 0.31982}{\mu^2 + 1.37544\mu + 0.487806} \tag{42}$$

A comparison of Figure 3a, f, or g to h shows that this approximation performs very well compared to those obtained from the GCC: the "walls" are at comparable values of μ. This is encouraging because the GCC require, in general, taking into account the external potential and the energy.

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Density functional approximations have been used for many years to correct models for missing short-range interaction.[14,15] Figure 4 shows the corrections provided for two approximations, the local density approximation, LDA, and that of Perdew, Burke, and Ernzerhof, PBE, modified to depend on μ.[15−17] The SAμs are around 1 bohr^{-1}, thus, improving over using only Kato's cusp condition (cf. Figure 3a). It may be at first surprising that in Figure 4 LDA is slightly better than PBE. However, PBE becomes better than LDA for small μ. This cannot be seen in Figure 4 because it shows only the region of "chemical accuracy"; the errors for small μ are much larger.

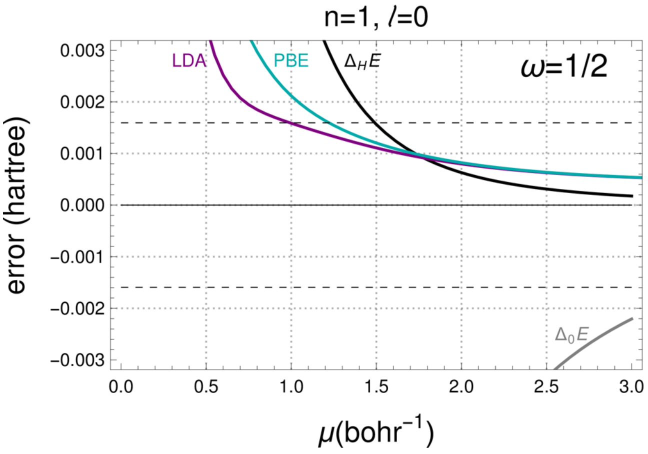

Figure 4. Errors in the ground state energy estimate for harmonium ($\omega = 1/2$) using density functional approximations (μ-LDA and μ-PBE). Also shown are the errors of the model energy, $\Delta_0 E(\mu)$, gray curve, and of the expectation value of the physical Hamiltonian, $\Delta_H E(\mu)$, black curve.

■ CONCLUSIONS

Summary. We have considered model systems, where electrons interact only via a long-range potential, eq 2. In order to obtain the physical energy we explored corrections based upon the short-range behavior of the wave function, both for the ground and excited states. The numerical results were all obtained for harmonium, eqs 16−22, where accurate results are easy to reach due to separability.

We are interested in having corrections to models where the interaction is very weak. However, the approximations proposed can be systematically improved in an asymptotic sense: as the order of the approximation increases, there is a domain of models close enough to the exact solution that gets systematically better. Unfortunately, at present, the approximations fail when the range of the interaction between particles becomes too large (our parameter μ becomes too small). We attribute it to imposing only the short-range behavior of the wave function. For short-range, the results turned out to be more reliable than obtained by correcting the models with density functional approximations. Unfortunately, the range of validity is system- and state-dependent.

Perspectives. In quantum chemistry there are different approaches to tackle the problem raised by the singularity of the Coulomb potential. A "brute force" pathway is to use a large expansion in Slater determinants. The burden can be reduced significantly by using "selected configuration interaction" techniques (see, e.g., ref 20 and references therein). Another way is to improve the description of the wave function by the use of correlation factors, like Jastrow factors in Quantum Monte Carlo (see, e.g., refs 21−24) or F12 methods (see, e.g., refs 25 and 26). Still another way to approach this problem is to use density functionals that transfer the short-range behavior from other systems (as a rule, from the uniform electron gas).

In this paper, we combine the spirit of the last two approaches. As in density functional calculations, we compute a model system for which the interaction has no singularity (and thus is expected to converge faster, in general). However, in contrast to density functional calculations, no density functional approximations are present, and the Hohenberg−Kohn theorem (formulated for ground states) is not used. The approach is applicable to ground and excited states.

As in methods using correlation factors we use the exact short-range behavior of the wave function. The trick allowing to use it comes from having a correction that depends only on the missing part of the interaction that is short-ranged.

The present paper did only show exploratory calculations. However, it is possible to extend considerations presented in this paper to other systems. Already Kurokawa et al.[8] have shown that the GCC can be applied when the Schrödinger equation for the relative coordinate cannot be separated from that of the center of mass (the He atom).

Before extending our approach there are several issues to be explored. Probably the first one is its formulation in terms of reduced density matrices. In this paper we use GCC for the wave function. To generalize our approach, it might be useful to express the GCC in terms of the 2RDM.[18,19]

One may ask whether it is not more convenient to re-express our formulation in terms of the 1RDM. In 1975 Kimball found a relationship between the 2RDM at coalescence and the distribution of momentum, in fact, the behavior of the 1RDM.[27] At the same time Yasuhara demonstrated that the energy of the uniform electron gas can be expressed in terms of the kinetic energy (one-particle operators) instead of the two-body interactions.[28] This gave rise to studies on using the adiabatic connection on the kinetic energy (i.e., the 1RDM) rather than on two-body interactions.[29−31] Recently, the effects of the electron−electron coalescence on the properties of the natural orbitals and structure of the 1RDM have been revealed.[32,33]

Another issue is the dependence of the GCC on the coalescence point.[6−9] For this, we can get inspiration from density functional approximation: in each point of space one has a different approximation. Even the Kato cusp condition (that seemingly is universal) contains a state dependence (through l). In density functional calculation it is treated by using the spin polarization,[34] but it can be treated in the context of a pair density (see, e.g., ref 35).

We illustrate the problematic with two two-electron harmonium systems (A and B) that instead of being treated separately are treated together (for example, having two quantum dots). The system may be described by a double-well potential with two wells sufficiently separated and deep, so that each of them can be approximated by a harmonic potential. We assume that this separation is large enough to neglect the exchange effects between electrons in A and B. Consequently, the spin part may be separated and, in effect, we can cosider the total wave function which depends on the orbital variables only. It can be written as a product of two harmonium wave functions:

$$\Psi_{\text{total}}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) = \Psi_A(\mathbf{r}_1, \mathbf{r}_2)\Psi_B(\mathbf{r}_3, \mathbf{r}_4) \quad (43)$$

Let us first consider that subsystem A is in a state with $l = 0$, while subsystem B is in a state with $l = 1$. In region A the coefficient $\tilde{c}_1 = 1/2$, while in region B, $\tilde{c}_1 = 1/4$. Let us now consider another example. In both subsystems we have $l = 0$. However, the values of ω differ: $\omega_A \neq \omega_B$. We can see from Figure 3a,f−h that the range of where results are reliable depend on the model chosen. For example, we see in Figure 3h that if we choose μ = 0.5 we will have chemical accuracy for a subsystem with $\omega = 1/4$, but that the error is significantly larger for a subsystem with ω = 1 where chemical accuracy is reached only for $\mu = 1$. Do we choose to make the more expensive global calculation, say with μ = 1, or do we decide to lose quality and make the cheaper calculation at $\mu = 1/2$? Alternatively, we might consider making calculations with models that change from one region of space to another.

In how far do we need to go beyond the Kato cusp condition? Using eq 42, Figure 3h, shows that this might not be needed. Furthermore, eq 50 of the Appendix (see also discussion in ref 11) shows that there are terms that are important when $r > 1/\mu$ even when r is small, and they may need a more careful treatment.

Another question is raised by analyzing the dependence on the external potential. It was shown by Kurokawa et al.[8] that for small interelectronic distance r, the leading term in the expansion of the Coulomb potential of the nuclei is quadratic. So, some of the conclusions drawn from the present treatment of harmonium might be applied in systems where the external potential is Coulombic.

APPENDIX: A DERIVATION OF EQ 30

We repeat here the argumentation given in ref 11, section III, where the result was obtained for $\lambda = 0$.

We consider the behavior of the Schrödinger equation

$$\left(-\frac{d^2}{dr^2} - \frac{2}{r}\frac{d}{dr} + \frac{(1-\lambda)\mathrm{erf}(\mu r) + \lambda}{r} + \frac{\omega^2 r^2}{2} - E\right)\psi(r) = 0 \tag{44}$$

at the limit of large μ. After a change of the variable r to $x = \mu r$ and defining $u(x) = \psi(x/\mu)$ one obtains

$$\left(-\frac{d^2}{dx^2} - \frac{2}{x}\frac{d}{dx} + \frac{(1-\lambda)\mathrm{erf}(x) + \lambda}{\mu x} + \frac{\omega^2 x^2}{2\mu^4} - \frac{E}{\mu^2}\right)u(x) = 0 \tag{45}$$

For large μ, we neglect terms proportional to $(1/\mu)^n$ with $n > 1$ and to the resulting equation apply perturbation theory up to the first order in $1/\mu$. We set

$$u(x) = u^{(0)}(x) + \frac{1}{\mu}u^{(1)}(x) \tag{46}$$

The 0th order in $1/\mu$ gives

$$\left(-\frac{d^2}{dx^2} - \frac{2}{x}\frac{d}{dx}\right)u^{(0)}(x) = 0 \tag{47}$$

From here we get

$$u^0(x) = \mathcal{A}_0 + \frac{\mathcal{A}_1}{x} \tag{48}$$

where $\mathcal{A}_0$ and $\mathcal{A}_1$ are integration constants. The wave function has to be finite at $x = 0$. Therefore, $\mathcal{A}_1 = 0$. Furthermore, as $u^{(0)}$ corresponds to the solution at $\mu = \infty$, namely, to the exact solution independent of either λ or μ, we set $\mathcal{A}_0 = \mathcal{N}$. Consequently, the equation for $u^{(1)}(x)$ is

$$\left(-\frac{d^2}{dx^2} - \frac{2}{x}\frac{d}{dx}\right)u^{(1)}(x) + \frac{(1-\lambda)\mathrm{erf}(x) + \lambda}{x}\mathcal{N} = 0 \tag{49}$$

After solving this equation and changing variable x to r, we get

$$\psi(r) = \mathcal{N}\left(1 + \frac{\lambda}{2}r + \frac{1-\lambda}{2\sqrt{\pi}\mu}e^{-\mu^2 r^2} + (1-\lambda)\left(\frac{r}{2} + \frac{1}{4\mu^2 r}\right)\mathrm{erf}(\mu r)\right) + \mathcal{B}_0 + \frac{\mathcal{B}_1}{\mu r} \tag{50}$$

where $\mathcal{B}_0$ and $\mathcal{B}_1$ are integration constants. To avoid singularity of the wave function at $r = 0$, $\mathcal{B}_1 = 0$. In order to recover results for $\lambda = 0$[11] we have to set $\mathcal{B}_0 = 0$. Finally, in the limit $r \to 0$, up to the first-order in $1/\mu$, we have

$$\psi(r)|_{r=0} = \mathcal{N}\left(1 + \frac{1-\lambda}{\sqrt{\pi}\mu}\right) \tag{51}$$

where $\mathcal{N}$ is a normalization constant independent of either λ or μ.

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Notes

The authors declare no competing financial interest.

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