

# Analytic First Derivatives for Explicitly Correlated, Multicenter, Gaussian Geminals

D. W. GILMORE,<sup>1</sup> P. M. KOZLOWSKI,<sup>2</sup> D. B. KINGHORN,<sup>1</sup>  
L. ADAMOWICZ<sup>1</sup>

<sup>1</sup>Department of Chemistry, University of Arizona, Tucson, Arizona 85721

<sup>2</sup>Department of Chemistry, Princeton University, Princeton, New Jersey 08544

Received 5 September 1996; revised 21 January 1997; accepted 23 January 1997

**ABSTRACT:** Variational calculations utilizing the analytic gradient of explicitly correlated Gaussian molecular integrals are presented for the ground state of the hydrogen molecule. Preliminary results serve to motivate the need for general formulas for analytic first derivatives of molecular integrals involving multicenter, explicitly correlated Gaussian geminals with respect to Gaussian exponents and coordinates of the orbital centers. Explicit formulas for analytic first derivatives of Gaussian functions containing correlation factors of the form  $\exp(-\beta r_{ij}^2)$  are derived and discussed. © 1997 John Wiley & Sons, Inc. Int J Quant Chem 63: 991–999, 1997

## Introduction

The idea of including explicitly interparticular distances in variational wave functions has a long history in quantum chemistry. It appears in the early work of Hylleraas [1], James and Coolidge [2], and in some of the most accurate studies for the H<sub>2</sub> molecule by Kolos and Wolniewicz [3]. It is generally accepted that Hylleraas-type expansions give the most accurate description of two- and three-electron systems, as well as reproducing the

electron-cusp correctly. The difficulty of extending the Hylleraas expansion for larger systems lies in the complexity of the required integrals, both in their analytical derivation and computational implementation (see, e.g., [4, 5]). The basis set of explicitly correlated Gaussians (ECG) proposed by Boys [6] and Singer [7] mitigate this problem with all the required integrals having closed analytic forms [8–10]. Since the introductory work of Boys and Singer, basis sets of ECG functions, in particular, Gaussian geminals (GG), have been applied to many different chemically and physically significant problems. An extensive bibliography on ECGs may be found in [11] and [9]. Very recent applications constitute the nonadiabatic studies of small systems [12, 13] and accurate multiple-moment

Correspondence to: L. Adamowicz.  
Contract grant sponsor: National Science Foundation.  
Contract grant number: CHE-9300497.

calculations for  $H_2$  and  $D_2$  [14]. In all applications of GGs, careful optimization of the nonlinear parameters is essential to obtain high-quality results. Although ECGs do not possess correct behavior near singularities, one may expect that long and well-optimized expansions should reproduce the cusp reasonably well. Recent studies presented by Cencek and Rychlewski [15] support this contention and place application of ECGs in a new perspective. These authors use a wave function expanded in terms of ECGs for the ground state of  $H_2$  at  $R = 1.4011$  au internuclear separation. When this molecular system is adjusted to  $R = 1.4$  au, one obtains an energy better than the one corresponding to the generalized James and Coolidge expansion. Liu and Hagstrom [16], and more recently Kolos [17], suggested that the generalized James-Coolidge expansion may not have been sufficiently flexible and therefore would not have converged to the true Born-Oppenheimer energy.

These results encourage further study of ECGs and show that the quality of results obtained can be comparable to Hylleraas-type implementations. Moreover, with the relatively simple evaluation of molecular, two-electron integrals, application of ECGs does not suffer from restriction to few-electron systems as do methods employing Hylleraas functions.

In most applications of GGs, or other types of ECGs, the optimization of the nonlinear parameters was achieved using numerical methods such as Powell's conjugate gradient method [18]. Other optimization methods have been based on tempering procedures [19–22] where the Gaussian exponents were generated as a sequence of parameters with only a few of the variables being optimized. It is surprising that standard optimization techniques based on analytical derivatives, widely used in other areas of quantum chemistry, were only just applied to correlated Gaussians quite recently [10, 23, 24]. In our previous works, we developed analytical first and second derivatives in conjunction with nonadiabatic, few-body calculations [10, 23]. In our present work, we continued this research direction by considering the problem of calculating first derivatives of multicenter, two-electron integrals for use in variational Born-Oppenheimer calculations.

The object of this article was to present the derivation of analytical first derivatives for multi-center GGs and to propose the possibility of using them in variational calculations. The existing code for the evaluation of integrals can be easily modi-

fied to obtain appropriate formulas for analytical derivatives of the integrals with respect to the parameters in the basis functions. The final section of this article contains preliminary numerical calculations for the ground state of the hydrogen molecule utilizing analytic first derivatives of the Rayleigh energy functional with respect to linear and nonlinear parameters of the wave function.

## Basic Properties of Gaussian Geminis

Analytical differentiation of an energy functional requires the evaluation of appropriate derivatives of molecular integrals with respect to the nonlinear parameters. Three different types of derivatives will be considered: those with respect to orbital exponents, correlation exponents, and orbital centers. In this section, we discuss the basic properties of GGs that are important for the derivation of analytical first derivatives. It should be pointed out that analytical derivatives, expressed in terms of GGs, can be rather long and complicated. We would like to keep the main body of the article as simple as possible; to that extent, let us introduce the following notation for a one-dimensional Cartesian Gaussian:

$$g(l^\mu, x, R_x^\mu, \alpha^\mu) = (x - R_x^\mu)^{l^\mu} \exp(-\alpha^\mu |x - R_x^\mu|^2); \quad (1)$$

thus, for a general Cartesian Gaussian, we have

$$\begin{aligned} G(l^\mu, m^\mu, n^\mu, \mathbf{r}, \mathbf{R}^\mu, \alpha^\mu) &= g(l^\mu, x, R_x^\mu, \alpha^\mu) g(m^\mu, y, R_y^\mu, \alpha^\mu) \\ &\times g(n^\mu, z, R_z^\mu, \alpha^\mu), \end{aligned} \quad (2)$$

and, finally, for a Cartesian GG,

$$\begin{aligned} \phi(l_1^\mu, m_1^\mu, n_1^\mu, l_2^\mu, m_2^\mu, n_2^\mu; \mathbf{R}_1^\mu, \mathbf{R}_2^\mu) &= G(l_1^\mu, m_1^\mu, n_1^\mu, \mathbf{r}_1, \mathbf{R}_1^\mu, \alpha_1^\mu) \\ &\times G(l_2^\mu, m_2^\mu, n_2^\mu, \mathbf{r}_2, \mathbf{R}_2^\mu, \alpha_2^\mu) \exp(-\beta_{12}^\mu \mathbf{r}_{12}^2). \end{aligned} \quad (3)$$

Alternatively, the last equation can be rewritten as a product of three two-dimensional GGs:

$$\begin{aligned} \phi(l_1^\mu, m_1^\mu, n_1^\mu, l_2^\mu, m_2^\mu, n_2^\mu; \mathbf{R}_1^\mu, \mathbf{R}_2^\mu) &= \phi(l_1^\mu, l_2^\mu; R_{1,x}^\mu, R_{2,x}^\mu) \phi(m_1^\mu, m_2^\mu; R_{1,y}^\mu, R_{2,y}^\mu) \\ &\times \phi(n_1^\mu, n_2^\mu; R_{1,z}^\mu, R_{2,z}^\mu), \end{aligned} \quad (4)$$

where, e.g., the  $x$ -component is given as

$$\begin{aligned}\phi(l_1^\mu, l_2^\mu; R_{1,x}^\mu, R_{2,x}^\mu) \\ = g(l_1^\mu, x_1, R_{1,x}^\mu, \alpha_1^\mu)g(l_2^\mu, x_2, R_{2,x}^\mu, \alpha_2^\mu) \\ \times \exp[-\beta_{12}^\mu(x_1 - x_2)^2].\end{aligned}$$

The general expression for analytical derivatives of molecular integrals with respect to orbital exponents, correlation exponents, or orbital centers can be obtained by direct differentiation of general formulas for GG integrals. Before we demonstrate this expressly, let us examine the result of differentiating a GG with respect to nonlinear parameters. Examination of the result of differentiation of the GG with respect to orbital exponents, which can be expressed in terms of products involving one-dimensional Gaussians, yields

$$\begin{aligned}\frac{\partial}{\partial \alpha_1^\mu} \phi(l_1^\mu, m_1^\mu, n_1^\mu, l_2^\mu, m_2^\mu, n_2^\mu; \mathbf{R}_1^\mu, \mathbf{R}_2^\mu) \\ = -[g(l_1^\mu + 2, x_1, R_{1,x}^\mu, \alpha_1^\mu) \\ \times g(m_1^\mu, y_1, R_{1,y}^\mu, \alpha_1^\mu)g(n_1^\mu, z_1, R_{1,z}^\mu, \alpha_1^\mu) \\ + g(l_1^\mu, x_1, R_{1,x}^\mu, \alpha_1^\mu) \\ \times g(m_1^\mu + 2, y_1, R_{1,y}^\mu, \alpha_1^\mu)g(n_1^\mu, z_1, R_{1,z}^\mu, \alpha_1^\mu) \\ + g(l_1^\mu, x_1, R_{1,x}^\mu, \alpha_1^\mu) \\ \times g(m_1^\mu, y_1, R_{1,y}^\mu, \alpha_1^\mu)g(n_1^\mu + 2, z_1, R_{1,z}^\mu, \alpha_1^\mu)] \\ \times G(l_2^\mu, m_2^\mu, n_2^\mu, \mathbf{r}_2, \mathbf{R}_2^\mu, \alpha_2^\mu) \exp(-\beta_{12}^\mu \mathbf{r}_{12}^2).\end{aligned}\quad (5)$$

The derivative with respect to correlation exponents,

$$\begin{aligned}\frac{\partial}{\partial \beta_{12}^\mu} \phi(l_1^\mu, m_1^\mu, n_1^\mu, l_2^\mu, m_2^\mu, n_2^\mu; \mathbf{R}_1^\mu, \mathbf{R}_2^\mu) \\ = -r_{12}^2 \phi(l_1^\mu, m_1^\mu, n_1^\mu, l_2^\mu, m_2^\mu, n_2^\mu; \mathbf{R}_1^\mu, \mathbf{R}_2^\mu),\end{aligned}\quad (6)$$

has a rather simple form. This becomes a little more complicated when one wishes to replace the right-hand side of the last equation by the appropriate combination of Cartesian Gaussians. To demonstrate this, recall that  $xg(l^\mu, x, R_x^\mu, \alpha^\mu)$  can be rewritten as a sum of two Gaussians:

$$\begin{aligned}xg(l^\mu, x, R_x^\mu, \alpha^\mu) = g(l^\mu + 1, x, R_x^\mu, \alpha^\mu) \\ + R_x^\mu g(l^\mu, x, R_x^\mu, \alpha^\mu).\end{aligned}\quad (7)$$

Multiple application of the above operation to the derivative with respect to correlation exponents leads to the following (for brevity, we demonstrate only the  $x$ -component of this expression):

$$\begin{aligned}(x_2 - x_1)^2 \phi(l_1^\mu, m_1^\mu, n_1^\mu, l_2^\mu, m_2^\mu, n_2^\mu; \mathbf{R}_1^\mu, \mathbf{R}_2^\mu) \\ = [\phi(l_1^\mu + 2, l_2^\mu; R_{1,x}^\mu, R_{2,x}^\mu) \\ - 2\phi(l_1^\mu + 1, l_2^\mu + 1; R_{1,x}^\mu, R_{2,x}^\mu) \\ + \phi(l_1^\mu, l_2^\mu + 2; R_{1,x}^\mu, R_{2,x}^\mu) \\ + 2(R_{1,x}^\mu - R_{2,x}^\mu)\phi(l_1^\mu + 1, l_2^\mu; R_{1,x}^\mu, R_{2,x}^\mu) \\ + 2(R_{2,x}^\mu - R_{1,x}^\mu)\phi(l_1^\mu, l_2^\mu + 1; R_{1,x}^\mu, R_{2,x}^\mu) \\ + (R_{1,x}^\mu - R_{2,x}^\mu)^2 \phi(l_1^\mu, l_2^\mu; R_{1,x}^\mu, R_{2,x}^\mu)] \\ \times \phi(m_1^\mu, m_2^\mu; R_{1,y}^\mu, R_{2,y}^\mu) \\ \times \phi(n_1^\mu, n_2^\mu; R_{1,z}^\mu, R_{2,z}^\mu).\end{aligned}\quad (8)$$

The last derivative, to be considered in this section, is that with respect to the orbital centers:

$$\begin{aligned}\frac{\partial}{\partial R_{1,x}^\mu} \phi(l_1^\mu, m_1^\mu, n_1^\mu, l_2^\mu, m_2^\mu, n_2^\mu; \mathbf{R}_1^\mu, \mathbf{R}_2^\mu) \\ = [2\alpha_1^\mu g(l_1^\mu + 1, x_1, R_{1,y}^\mu, \alpha_1^\mu) \\ - l_1^\mu g(l_1^\mu - 1, x_1, R_{1,x}^\mu, \alpha_1^\mu)] \\ \times g(m_1^\mu, y_1, R_{1,y}^\mu, \alpha_1^\mu)g(n_1^\mu, z_1, R_{1,z}^\mu, \alpha_1^\mu) \\ \times G(l_2^\mu, m_2^\mu, n_2^\mu, \mathbf{r}_2, \mathbf{R}_2^\mu, \alpha_2^\mu) \exp(-\beta_{12}^\mu \mathbf{r}_{12}^2).\end{aligned}\quad (9)$$

Let us summarize some of properties of interest for GGs which are helpful for the generation of analytical derivatives. Let  $\mathbf{R}^{\mu\nu}$  denote the third common center of two Gaussians as

$$\mathbf{R}^{\mu\nu} = \frac{\alpha^\mu \mathbf{R}^\mu + \alpha^\nu \mathbf{R}^\nu}{\alpha^\mu + \alpha^\nu}. \quad (10)$$

The product of two Gaussian can be expressed as

$$\begin{aligned}\phi(0, 0, 0, 0; \mathbf{R}_1^\mu, \mathbf{R}_2^\mu)\phi(0, 0, 0, 0; \mathbf{R}_1^\nu, \mathbf{R}_2^\nu) \\ = K_{\mu\nu} \phi(0, 0, 0, 0; \mathbf{R}_1^{\mu\nu}, \mathbf{R}_2^{\mu\nu}),\end{aligned}\quad (11)$$

with  $K_{\mu\nu}$  represented as

$$K_{\mu\nu} = \exp\left(-\sum_{i=1}^2 \frac{\alpha_i^\mu \alpha_i^\nu}{\alpha_i^\mu + \alpha_i^\nu} |\mathbf{R}_i^\mu - \mathbf{R}_i^\nu|^2\right). \quad (12)$$

For a general Cartesian Gaussian, expansion of the polynomial of coordinates and center positions with respect to the common centers yields

$$(x_p - R_p^\mu)^{l_p^\mu} (x_p - R_p^\nu)^{l_p^\nu} = \sum_i f_i(l_p^\mu, l_p^\nu, R_{p,x}^{\mu\nu} R_{p,x}^{\mu}, R_{p,x}^{\mu\nu} R_{p,x}^{\nu}) \times (x_p - R_{p,x}^{\mu\nu})^i, \quad (13)$$

with

$$f_i(l, m, a, b) = \sum_{i=\max\{0, j-m\}}^{\min\{j, l\}} \binom{l}{i} \binom{m}{j-i} a^{l-i} b^{m+i-j} \quad (14)$$

and

$$\overline{R_{p,x}^{\mu\nu} R_{p,x}^{\mu}} = R_{p,x}^{\mu\nu} - R_{p,x}^{\mu}. \quad (15)$$

The final product takes the following form:

$$\begin{aligned} & \phi(l_1^\mu, l_2^\mu; R_{1,x}^\mu, R_{2,x}^\mu) \phi(l_1^\nu, l_2^\nu; R_{1,x}^\nu, R_{2,x}^\nu) \\ &= K_{\mu\nu}^x \sum_{i_1} \sum_{i_2} f_{i_1} f_{i_2} \phi(i_1, i_2; R_{1,x}^{\mu\nu}, R_{2,x}^{\mu\nu}), \end{aligned} \quad (16)$$

where, for simplicity, only the  $x$ -component has been shown.

### Analytical Derivatives of Molecular Integrals

To demonstrate the analytical differentiation of molecular integrals over GGs, consider integrals of the following form:

$$O_{\mu\nu} = \iint \phi(l_1^\mu, m_1^\mu, n_1^\mu, l_2^\mu, m_2^\mu, n_2^\mu; \mathbf{R}_1^\mu, \mathbf{R}_2^\mu) \times \hat{\phi}(l_1^\nu, m_1^\nu, n_1^\nu, l_2^\nu, m_2^\nu, n_2^\nu; \mathbf{R}_1^\nu, \mathbf{R}_2^\nu) d\mathbf{r}_1 d\mathbf{r}_2. \quad (17)$$

Suppose that we would like to calculate derivatives of the above integral with respect to  $\xi^\mu$ , ( $\xi = \alpha_1^\mu, \alpha_2^\mu, \beta_{12}^\mu, R_{1,x}^\mu, \dots$ ). These can be obtained

as follows:

$$\begin{aligned} & \frac{\partial O_{\mu\nu}}{\partial \xi^\mu} \\ &= \iint \left( \frac{\partial}{\partial \xi^\mu} \phi(l_1^\mu, m_1^\mu, n_1^\mu, l_2^\mu, m_2^\mu, n_2^\mu; \mathbf{R}_1^\mu, \mathbf{R}_2^\mu) \right) \\ & \times \hat{\phi}(l_1^\nu, m_1^\nu, n_1^\nu, l_2^\nu, m_2^\nu, n_2^\nu; \mathbf{R}_1^\nu, \mathbf{R}_2^\nu) d\mathbf{r}_1 d\mathbf{r}_2. \end{aligned} \quad (18)$$

This procedure can be applied to the overlap integral, nuclear attraction integral, and electron repulsion integral; however, it cannot be applied directly to the kinetic energy. The kinetic energy integral must first be expressed in terms of overlap integrals, thereby permitting the straightforward implementation of the above procedure.

### OVERLAP INTEGRAL

The overlap integral over GGs can be expressed as a product of three two-dimensional overlap integrals:

$$\langle \phi_\mu | \phi_\nu \rangle = \langle l_1^\mu, l_2^\mu | l_1^\nu, l_2^\nu \rangle \langle m_1^\mu, m_2^\mu | m_1^\nu, m_2^\nu \rangle \times \langle n_1^\mu, n_2^\mu | n_1^\nu, n_2^\nu \rangle, \quad (19)$$

where these overlap integrals are represented as

$$\langle l_1^\mu, l_2^\mu | l_1^\nu, l_2^\nu \rangle = \langle 0, 0 | 0, 0 \rangle \sum_{i_1, i_2, r_1, r_2, u} A_{i_1, i_2, r_1, r_2, u}, \quad (20)$$

with the spherical component of the overlap integral expressed as

$$\langle 0, 0 | 0, 0 \rangle = \frac{\pi K_{\mu\nu}^x}{\sqrt{a_1^{\mu\nu} a_2^{\mu\nu} + \beta_{12}^{\mu\nu} (a_1^{\mu\nu} + a_2^{\mu\nu})}}, \quad (21)$$

where  $K_{\mu\nu}^x$  is given in Eq. (12) and the Cartesian components as

$$\begin{aligned} & A_{i_1, i_2, r_1, r_2, u} \\ &= (-)^{i_1+u} f_{i_1}(l_1^\mu, l_1^\nu, R_{1,x}^{\mu\nu} R_{1,x}^\mu, R_{1,x}^{\mu\nu} R_{1,x}^\nu) \\ & \times f_{i_2}(l_2^\mu, l_2^\nu, R_{2,x}^{\mu\nu} R_{2,x}^\mu, R_{2,x}^{\mu\nu} R_{2,x}^\nu) C_{r_1}^{i_1} C_{r_2}^{i_2} \\ & \times \left( \frac{a_1^{\mu\nu} a_2^{\mu\nu} + \beta_{12}^{\mu\nu} (a_1^{\mu\nu} + a_2^{\mu\nu})}{4 a_1^{\mu\nu} a_2^{\mu\nu} \beta_{12}^{\mu\nu}} \right)^{2(r_1+r_2)+u-i_1-i_2} \\ & \times (R_{1,x}^{\mu\nu} R_{2,x}^{\mu\nu})^{i_1+i_2-2(r_1+r_2+u)}, \end{aligned} \quad (22)$$

where

$$C_m^n = \frac{n!}{2^n \alpha^{n-m} m! (n-2m)!}. \quad (23)$$

Using the prescriptions for derivatives of GGs presented previously, the derivatives with respect to orbital exponents are obtained:

$$\begin{aligned} \frac{\partial \langle \phi_\mu | \phi_\nu \rangle}{\partial \alpha_1^\mu} &= - [\langle l_1^\mu + 2, l_2^\mu | l_1^\nu, l_2^\nu \rangle \langle m_1^\mu, m_2^\mu | m_1^\nu, m_2^\nu \rangle \\ &\quad \times \langle n_1^\mu, n_2^\mu | n_1^\nu, n_2^\nu \rangle + \langle l_1^\mu, l_2^\mu | l_1^\nu, l_2^\nu \rangle \\ &\quad \times \langle m_1^\mu + 2, m_2^\mu | m_1^\nu, m_2^\nu \rangle \langle n_1^\mu, n_2^\mu | n_1^\nu, n_2^\nu \rangle \\ &\quad + \langle l_1^\mu, l_2^\mu | l_1^\nu, l_2^\nu \rangle \langle m_1^\mu, m_2^\mu | m_1^\nu, m_2^\nu \rangle \\ &\quad \times \langle n_1^\mu + 2, n_2^\mu | n_1^\nu, n_2^\nu \rangle], \end{aligned} \quad (24)$$

and in a similar fashion, derivatives with respect to the correlation exponent,

$$\begin{aligned} \frac{\partial \langle \phi_\mu | \phi_\nu \rangle}{\partial \beta_{12}^\mu} &= - [\langle l_1^\mu + 2, l_2^\mu | l_1^\nu, l_2^\nu \rangle \\ &\quad - 2 \langle l_1^\mu + 1, l_2^\mu + 1 | l_1^\nu, l_2^\nu \rangle + \langle l_1^\mu, l_2^\mu + 2 | l_1^\nu, l_2^\nu \rangle \\ &\quad + 2(R_{1,x}^\mu - R_{2,x}^\mu) \langle l_1^\mu + 1, l_2^\mu | l_1^\nu, l_2^\nu \rangle \\ &\quad + 2(R_{2,x}^\mu - R_{1,x}^\mu) \langle l_1^\mu, l_2^\mu + 1 | l_1^\nu, l_2^\nu \rangle \\ &\quad + (R_{1,x}^\mu - R_{2,x}^\mu)^2 \langle l_1^\mu, l_2^\mu | l_1^\nu, l_2^\nu \rangle] \\ &\quad \times \langle m_1^\mu, m_2^\mu | m_1^\nu, m_2^\nu \rangle \langle n_1^\mu, n_2^\mu | n_1^\nu, n_2^\nu \rangle \\ &\quad + y_{comp} + z_{comp}. \end{aligned} \quad (25)$$

Partial differentiation with respect to the orbital center can be performed in the following manner:

$$\begin{aligned} \frac{\partial \langle \phi_\mu | \phi_\nu \rangle}{\partial R_{1,x}^\mu} &= [2\alpha_1^\mu \langle l_1^\mu + 1, l_2^\mu | l_1^\nu, l_2^\nu \rangle - l_1^\mu \langle l_1^\mu, l_2^\mu | l_1^\nu, l_2^\nu \rangle] \\ &\quad \times \langle m_1^\mu, m_2^\mu | m_1^\nu, m_2^\nu \rangle \langle n_1^\mu, n_2^\mu | n_1^\nu, n_2^\nu \rangle. \end{aligned} \quad (26)$$

This method is extensible to derivatives with respect to other orbital centers as well.

### KINETIC-ENERGY INTEGRAL

The kinetic energy matrix element can be considered as a sum of two components:

$$\langle T^{\mu\nu} \rangle = \langle T_1^{\mu\nu} \rangle + \langle T_2^{\mu\nu} \rangle, \quad (27)$$

where the first component has, e.g., the following form:

$$\begin{aligned} 2\langle T_1^{\mu\nu} \rangle &= - \iint \phi(l_1^\mu, m_1^\mu, n_1^\mu, l_2^\mu, m_2^\mu, n_2^\mu; \mathbf{R}_1^\mu, \mathbf{R}_2^\mu) \\ &\quad \times \nabla_1^2 \phi(l_1^\nu, m_1^\nu, n_1^\nu, l_2^\nu, m_2^\nu, n_2^\nu; \mathbf{R}_1^\nu, \mathbf{R}_2^\nu) d\mathbf{r}_1 d\mathbf{r}_2. \end{aligned} \quad (28)$$

This last equation cannot be differentiated directly, as previously discussed. We must first find an expression in terms of overlap integrals, whose derivatives are easily managed. To demonstrate this, let us transform the kinetic energy integral using Green's theorem [8]:

$$\begin{aligned} 2\langle T_1^{\mu\nu} \rangle &= \int d\mathbf{r}_2 G(l_2^\mu, m_2^\mu, n_2^\mu, \mathbf{r}_2, \mathbf{R}_2^\mu, \alpha_2^\mu) \\ &\quad \times G(l_2^\nu, m_2^\nu, n_2^\nu, \mathbf{r}_2, \mathbf{R}_2^\nu, \alpha_2^\nu) \\ &\quad \times \int d\mathbf{r}_1 \{ 4\beta_{12}^\mu \beta_{12}^\nu r_{12}^2 G(l_1^\mu, m_1^\mu, n_1^\mu, \mathbf{r}_1, \mathbf{R}_1^\mu, \alpha_1^\mu) \\ &\quad \times G(l_1^\nu, m_1^\nu, n_1^\nu, \mathbf{r}_1, \mathbf{R}_1^\nu, \alpha_1^\nu) \\ &\quad - (\beta_{12}^\mu + \beta_{12}^\nu)^{-1} W(\mathbf{r}_1) \} \\ &\quad \times \exp[-(\beta_{12}^\mu + \beta_{12}^\nu)r_{12}^2], \end{aligned} \quad (29)$$

where

$$\begin{aligned} W(\mathbf{r}_1) &= \left( \frac{\beta_{12}^\nu}{\beta_{12}^\mu + \beta_{12}^\nu} \right) G(l_1^\nu, m_1^\nu, n_1^\nu, \mathbf{r}_1, \mathbf{R}_1^\nu, \alpha_1^\nu) \\ &\quad \times \nabla_1^2 G(l_1^\mu, m_1^\mu, n_1^\mu, \mathbf{r}_1, \mathbf{R}_1^\mu, \alpha_1^\mu) \\ &\quad + \left( \frac{\beta_{12}^\mu}{\beta_{12}^\mu + \beta_{12}^\nu} \right) G(l_1^\mu, m_1^\mu, n_1^\mu, \mathbf{r}_1, \mathbf{R}_1^\mu, \alpha_1^\mu) \\ &\quad \times \nabla_1^2 G(l_1^\nu, m_1^\nu, n_1^\nu, \mathbf{r}_1, \mathbf{R}_1^\nu, \alpha_1^\nu). \end{aligned} \quad (30)$$

This formula is valid for  $\{\beta_{12}^\mu = 0, \beta_{12}^\nu \neq 0\}$ , or  $\{\beta_{12}^\mu \neq 0, \beta_{12}^\nu = 0\}$  and additionally holds for  $\{\beta_{12}^\mu = \beta_{12}^\nu = 0\}$ . In the latter case, it can be shown that  $\beta_{12}^\mu/(\beta_{12}^\mu + \beta_{12}^\nu)$  and  $\beta_{12}^\nu/(\beta_{12}^\mu + \beta_{12}^\nu)$  must be replaced by  $(\frac{1}{2})$ . The first term in the expression for the kinetic energy, as shown above, can be expressed as

$$\begin{aligned} 2\langle T_1^{\mu\nu} \rangle &= 4\beta_{12}^\mu \beta_{12}^\nu [\langle l_1^\mu + 2, l_2^\mu | l_1^\nu, l_2^\nu \rangle \\ &\quad - 2\langle l_1^\mu + 1, l_2^\mu + 1 | l_1^\nu, l_2^\nu \rangle \\ &\quad + \langle l_1^\mu, l_2^\mu + 2 | l_1^\nu, l_2^\nu \rangle] \end{aligned}$$

$$\begin{aligned}
& + 2(R_{1,x}^\mu - R_{2,x}^\mu) \langle l_1^\mu + 1, l_2^\mu | l_1^\nu, l_2^\nu \rangle \\
& + 2(R_{2,x}^\mu - R_{1,x}^\mu) \langle l_1^\mu, l_2^\mu + 1 | l_1^\nu, l_2^\nu \rangle \\
& + (R_{1,x}^\mu - R_{2,x}^\mu)^2 \langle l_1^\mu, l_2^\mu | l_1^\nu, l_2^\nu \rangle \\
& \times \langle m_1^\mu, m_2^\mu | m_1^\nu, m_2^\nu \rangle \langle n_1^\mu, n_2^\mu | n_1^\nu, n_2^\nu \rangle \\
& + 4\beta_{12}^\mu \beta_{12}^\nu y_{comp} + 4\beta_{12}^\mu \beta_{12}^\nu z_{comp} \\
& \times \int d\mathbf{r}_2 G(l_2^\mu, m_2^\mu, n_2^\mu, \mathbf{r}_2, \mathbf{R}_2^\mu, \alpha_2^\mu) \\
& \times G(l_2^\nu, m_2^\nu, n_2^\nu, \mathbf{r}_2, \mathbf{R}_2^\nu, \alpha_2^\nu) \\
& \times \int d\mathbf{r}_1 \{ -(\beta_{12}^\mu + \beta_{12}^\nu)^{-1} W(\mathbf{r}_1) \} \\
& \times \exp[-(\beta_{12}^\mu + \beta_{12}^\nu)r_{12}^2], \quad (31)
\end{aligned}$$

where, for brevity, again only the  $x$ -component has been shown. One now obtains

$$\begin{aligned}
& \nabla_1^2 G(l_1^\mu, m_1^\mu, n_1^\mu, \mathbf{r}_1, \mathbf{R}_1^\mu, \alpha_1^\mu) \\
& = -2\alpha_1^\mu [2(l_1^\mu + m_1^\mu + n_1^\mu) + 3] \\
& \times G(l_1^\mu, m_1^\mu, n_1^\mu, \mathbf{r}_1, \mathbf{R}_1^\mu, \alpha_1^\mu) \\
& - 4\alpha_1^\mu [G(l_1^\mu + 2, m_1^\mu, n_1^\mu, \mathbf{r}_1, \mathbf{R}_1^\mu, \alpha_1^\mu) \\
& + G(l_1^\mu, m_1^\mu + 2, n_1^\mu, \mathbf{r}_1, \mathbf{R}_1^\mu, \alpha_1^\mu) \\
& + G(l_1^\mu, m_1^\mu, n_1^\mu + 2, \mathbf{r}_1, \mathbf{R}_1^\mu, \alpha_1^\mu)] \\
& + l_1^\mu(l_1^\mu - 1)G(l_1^\mu - 2, m_1^\mu, n_1^\mu, \mathbf{r}_1, \mathbf{R}_1^\mu, \alpha_1^\mu) \\
& + m_1^\mu(m_1^\mu - 1)G(l_1^\mu, m_1^\mu - 2, n_1^\mu, \mathbf{r}_1, \mathbf{R}_1^\mu, \alpha_1^\mu) \\
& + n_1^\mu(n_1^\mu - 1)G(l_1^\mu, m_1^\mu, n_1^\mu - 2, \mathbf{r}_1, \mathbf{R}_1^\mu, \alpha_1^\mu). \quad (32)
\end{aligned}$$

Differentiation of the kinetic integral can now be easily expressed in terms of integrals of the overlap.

### NUCLEAR ATTRACTION INTEGRAL

The analytical derivatives of the nuclear attraction integrals and electron repulsion integrals can be evaluated in similar fashion; however, for economy of presentation, we will keep them in separate subsections. According to Lester and Krauss [8], the nuclear attraction integral has the generalized form

$$\langle \phi_\mu | \frac{1}{|\mathbf{r} - \mathbf{R}_E|} | \phi_\nu \rangle = B_0 \sum_{(I)} B_{(I)} \sum_{(J)} B_{(J)} \sum_{(K)} B_{(K)} F_\nu(Z_1), \quad (33)$$

which can be denoted as  $\langle l_1^\mu, l_2^\mu, m_1^\mu, m_2^\mu, n_1^\mu, n_2^\mu | 1/\mathbf{r} - \mathbf{R}_E | l_1^\nu, l_2^\nu, m_1^\nu, m_2^\nu, n_1^\nu, n_2^\nu \rangle$ . The derivative with respect to orbital exponents has the fol-

lowing form:

$$\begin{aligned}
& \frac{\partial}{\partial \alpha_1^\mu} \langle \phi_\mu | \frac{1}{|\mathbf{r} - \mathbf{R}_E|} | \phi_\nu \rangle \\
& = \langle l_1^\mu + 2, l_2^\mu, m_1^\mu, m_2^\mu, n_1^\mu, n_2^\mu | \frac{1}{|\mathbf{r} - \mathbf{R}_E|} \\
& \times |l_1^\mu, l_2^\mu, m_1^\mu, m_2^\mu, n_1^\mu, n_2^\mu \rangle \\
& \times \langle l_1^\mu, l_2^\mu, m_1^\mu + 2, m_2^\mu, n_1^\mu, n_2^\mu | \frac{1}{|\mathbf{r} - \mathbf{R}_E|} \\
& \times |l_1^\mu, l_2^\mu, m_1^\mu, m_2^\mu, n_1^\mu, n_2^\mu \rangle \\
& \times \langle l_1^\mu, l_2^\mu, m_1^\mu, m_2^\mu, n_1^\mu + 2, n_2^\mu | \frac{1}{|\mathbf{r} - \mathbf{R}_E|} \\
& \times |l_1^\mu, l_2^\mu, m_1^\mu, m_2^\mu, n_1^\mu, n_2^\mu \rangle. \quad (34)
\end{aligned}$$

Differentiation with respect to correlation exponents gives

$$\begin{aligned}
& \frac{\partial}{\partial \beta_{12}^\mu} \langle \phi_\mu | \frac{1}{|\mathbf{r} - \mathbf{R}_E|} | \phi_\nu \rangle \\
& = + \langle l_1^\mu + 2, l_2^\mu, m_1^\mu, m_2^\mu, n_1^\mu, n_2^\mu | \frac{1}{|\mathbf{r} - \mathbf{R}_E|} \\
& \times |l_1^\nu, l_2^\nu, m_1^\nu, m_2^\nu, n_1^\nu, n_2^\nu \rangle \\
& - 2 \langle l_1^\mu + 1, l_2^\mu + 1, m_1^\mu, m_2^\mu, n_1^\mu, n_2^\mu | \frac{1}{|\mathbf{r} - \mathbf{R}_E|} \\
& \times |l_1^\nu, l_2^\nu, m_1^\nu, m_2^\nu, n_1^\nu, n_2^\nu \rangle \\
& + \langle l_1^\mu, l_2^\mu + 2, m_1^\mu, m_2^\mu, n_1^\mu, n_2^\mu | \frac{1}{|\mathbf{r} - \mathbf{R}_E|} \\
& \times |l_1^\nu, l_2^\nu, m_1^\nu, m_2^\nu, n_1^\nu, n_2^\nu \rangle \\
& + 2(R_{1,x}^\mu - R_{2,x}^\mu) \langle l_1^\mu + 1, l_2^\mu, m_1^\mu, m_2^\mu, n_1^\mu, n_2^\mu | \\
& \times \frac{1}{|\mathbf{r} - \mathbf{R}_E|} |l_1^\nu, l_2^\nu, m_1^\nu, m_2^\nu, n_1^\nu, n_2^\nu \rangle \\
& + 2(R_{2,x}^\mu - R_{1,x}^\mu) \langle l_1^\mu, l_2^\mu + 1, m_1^\mu, m_2^\mu, n_1^\mu, n_2^\mu | \\
& \times \frac{1}{|\mathbf{r} - \mathbf{R}_E|} |l_1^\nu, l_2^\nu, m_1^\nu, m_2^\nu, n_1^\nu, n_2^\nu \rangle \\
& + (R_{1,x}^\mu - R_{2,x}^\mu)^2 \langle l_1^\mu, l_2^\mu, m_1^\mu, m_2^\mu, n_1^\mu, n_2^\mu | \\
& \times \frac{1}{|\mathbf{r} - \mathbf{R}_E|} |l_1^\nu, l_2^\nu, m_1^\nu, m_2^\nu, n_1^\nu, n_2^\nu \rangle \\
& + y_{comp} + z_{comp}. \quad (35)
\end{aligned}$$

The derivative with respect to orbital centers can now be obtained as

$$\begin{aligned} & \frac{\partial}{\partial R_{1,x}^{\mu}} \langle \phi_{\mu} | \frac{1}{|\mathbf{r} - \mathbf{R}_E|} | \phi_{\nu} \rangle \\ &= 2\alpha_1^{\mu} \langle l_1^{\mu} + 1, l_2^{\mu}, m_1^{\mu}, m_2^{\mu}, n_1^{\mu}, n_2^{\mu} | \frac{1}{|\mathbf{r} - \mathbf{R}_E|} \\ & \quad \times | l_1^{\mu}, l_2^{\mu}, m_1^{\mu}, m_2^{\mu}, n_1^{\mu}, n_2^{\mu} \rangle \\ & \quad - l_1^{\mu} \langle l_1^{\mu} - 1, l_2^{\mu}, m_1^{\mu}, m_2^{\mu}, n_1^{\mu}, n_2^{\mu} | \frac{1}{|\mathbf{r} - \mathbf{R}_E|} \\ & \quad \times | l_1^{\mu}, l_2^{\mu}, m_1^{\mu}, m_2^{\mu}, n_1^{\mu}, n_2^{\mu} \rangle. \end{aligned} \quad (36)$$

### ELECTRON REPULSION INTEGRAL

$$\langle \phi_{\mu} | \frac{1}{|\mathbf{r}_2 - \mathbf{r}_1|} | \phi_{\nu} \rangle = \sum_{(I)} C_{(I)} \sum_{(J)} C_{(J)} \sum_{(K)} C_{(K)} F_{\nu}(Z) \quad (37)$$

can be recast into a representation similar to the nuclear attraction integral:

$$\begin{aligned} & \langle l_1^{\mu}, l_2^{\mu}, m_1^{\mu}, m_2^{\mu}, n_1^{\mu}, n_2^{\mu} | \frac{1}{|\mathbf{r}_2 - \mathbf{r}_1|} \\ & \quad \times | l_1^{\mu}, l_2^{\mu}, m_1^{\mu}, m_2^{\mu}, n_1^{\mu}, n_2^{\mu} \rangle. \end{aligned} \quad (38)$$

The formulas derived above are quite valid for ER integrals after the appropriate exchange of  $1/|\mathbf{r} - \mathbf{R}_E|$  for  $1/|\mathbf{r}_2 - \mathbf{r}_1|$ . Such a procedure should be straightforward and need not be redundantly stated here.

---

### Numerical Results

A simple implementation of a gradient-based calculation for molecular hydrogen was performed. The preliminary results served to motivate the derivation of the above generalized formulas for analytic derivatives in the GG basis. In this section, we briefly describe how this gradient-optimization of the ground state of  $H_2$  was performed in a multicenter GG basis.

The form of the spatial part of the ground-state wave function used in the present calculations (properly symmetrized with respect to exchange of

identical particles) was

$$\begin{aligned} \Psi(1,2) = & \sum_{\mu=1}^n c_{\mu} (1 + P_{12}) (1 + P_{H_1 H_2}) \\ & \times \phi_{\mu}(0,0,0,0,0,0; R_A^{\mu}, R_B^{\mu}), \end{aligned} \quad (39)$$

where

$$\begin{aligned} & \phi_{\mu}(0,0,0,0,0,0; R_A^{\mu}, R_B^{\mu}) \\ &= e^{\alpha_1^{\mu} |\mathbf{r}_1 - \mathbf{R}_A|^2 - \alpha_2^{\mu} |\mathbf{r}_2 - \mathbf{R}_B|^2 - \beta_{12}^{\mu} |\mathbf{r}_1 - \mathbf{r}_2|^2} \end{aligned} \quad (40)$$

[see Eq. (3)],  $P_{12}$  represents the exchange of electrons, and  $P_{H_1 H_2}$  represents the exchange of nuclei.  $R_A$  and  $R_B$  are not necessarily assumed to represent the centers of the nuclei ( $R_{H_1}, R_{H_2}$ ). Nor should it be assumed that  $R_A = R_B$ .

The analytical derivatives of the GG molecular integrals were realized via "automatic differentiation" of the Fortran 90 program code with the aid of readily available software packages. The obtained algorithms fully agree with the expressions derived in the previous sections. The components of the analytical derivative were rigorously tested by finite differencing of the original program code.

Optimization occurs via minimization of the Rayleigh quotient:

$$E_{\text{Ground State}} = \min_{\{c, a\}} (E_{\text{Rayleigh}}), \quad (41)$$

$$E_{\text{Rayleigh}} = \frac{\langle \Psi(1,2) | \hat{H} | \Psi(1,2) \rangle}{\langle \Psi(1,2) | \Psi(1,2) \rangle} = \frac{c' H(a)c}{c' S(a)c}, \quad (42)$$

with respect to linear and nonlinear parameters, where the prime ('') indicates transposition;  $c$ , the linear parameters;  $a$ , the set of all nonlinear optimization parameters:  $\{\alpha_1^{\mu}, \alpha_2^{\mu}, \beta_{12}^{\mu}, R_1^{\mu}, R_2^{\mu}\}$ ;  $H$ , the Hamiltonian matrix; and  $S$ , the overlap matrix. The optimization is constrained by requiring that each GG is a square-integrable function, which condition is fulfilled when the determinant,

$$\det \begin{pmatrix} \alpha_1 + \beta_{12} & -\beta_{12} \\ -\beta_{12} & \alpha_2 + \beta_{12} \end{pmatrix} = \alpha_1^{\mu} \alpha_2^{\mu} + \beta_{12}^{\mu} (\alpha_1^{\mu} + \alpha_2^{\mu}), \quad (43)$$

remains positive [see Eq. (21)]. This is accomplished by utilizing the following relation:  $\det(t t') > 0$ , which is true for any lower-triangular,

full-rank matrix,

$$t = \begin{pmatrix} t_1 & 0 \\ t_3 & t_2 \end{pmatrix},$$

whose elements are not constrained (except for  $t_1 \neq 0$  and  $t_2 \neq 0$ ). This requires the following Cholesky decomposition:

$$tt' = \begin{pmatrix} \alpha_1 + \beta_{12} & -\beta_{12} \\ -\beta_{12} & \alpha_2 + \beta_{12} \end{pmatrix}.$$

From this equation, we obtain the following relations between  $\alpha_1$ ,  $\alpha_2$ ,  $\beta_{12}$  and  $t_1$ ,  $t_2$ ,  $t_3$ :

$$\alpha_1 = t_1^2 + t_1 t_3 \quad (44)$$

$$\alpha_2 = t_2^2 + t_3^2 + t_1 t_3 \quad (45)$$

$$\beta_{12} = -t_1 t_3. \quad (46)$$

Optimization proceeds with the substitution of the unconstrained variables  $\{t_1^{\mu}, t_2^{\mu}, t_3^{\mu}\}$  for the constrained ones  $\{\alpha_1^{\mu}, \alpha_2^{\mu}, \beta_{12}^{\mu}\}$ .

The differential with respect to the linear coefficients is given as

$$\partial E_{\text{linear}} = \frac{2c'(H - ES)\partial c}{c'Sc}. \quad (47)$$

The differential with respect to the nonlinear parameters is given as

$$\begin{aligned} \partial E_{\text{non-linear}} &= \frac{2c'(\partial H - E\partial S)c}{c'Sc} \\ &= (c \otimes c') \left( \frac{\partial \text{vec}H}{\partial d} - E \frac{\partial \text{vec}S}{\partial d} \right) \partial a, \end{aligned} \quad (48)$$

where the Kronecker product ( $\otimes$ ) and the matrix vectorization operator ( $\text{vec}$ ) were utilized as described by Kinghorn [25]. The nonzero terms in the matrix  $\partial \text{vec}H / \partial d$  are the partial derivatives with respect to all the nonlinear parameters in the basis (e.g., components such as  $\partial T_{\mu\nu} / \partial \alpha_1^{\mu}$ ). The right-hand side of Eq. (48) contains sparse matrices which were reassembled into a dense-matrix data structure [24] and numerically verified.

Several optimization algorithms were investigated, as is required by most nonlinear optimization problems. The method of choice was a "stochastic-growth, gradient minimization" algorithm in which the GG basis set was systematically grown from  $n = 1$  to  $n = 140$ . The IMSL DUMING,

"double-precision, multivariate, quasi-Newton, analytic gradient-based" optimization routine was employed with energy functional minimization proceeding to double-precision, machine-specific convergence criteria.

When the basis set is small, calculations proceed quite rapidly. When the basis set starts to become large, it has previously gone through several optimization iterations and is considered to be quite well optimized already. The result of this is that subsequent optimization steps require fewer iterations to achieve the convergence criteria.

The best GG literature result at present is  $-1.174475931$  obtained with 700 functions [26] and is represented by the horizontal line to which our convergence profile appears asymptotic in Figure 1. The results reported in Table I represent 17 of the 141 stochastic-growth iterations which were performed. These points were selected based upon the consideration of having converged very well relative to the remaining iterations.

We do not report a new bound on the GG calculation of molecular hydrogen. Instead, we have presented a rudimentary implementation of an analytic-gradient optimization which preliminarily shows a rapidly convergent method of con-

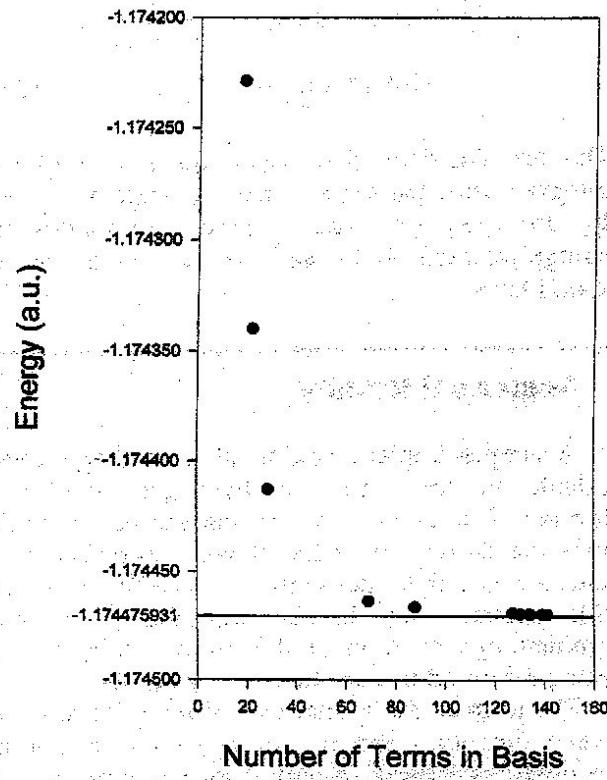


FIGURE 1. Energy convergence for  $H_2$ .

**TABLE I**  
Energy convergence.

No. of Terms:	Energy (a.u.)
1	-1.080169666
2	-1.143496255
4	-1.163729386
5	-1.168108498
6	-1.170809640
8	-1.172575881
11	-1.173645044
18	-1.174228757
22	-1.174339602
29	-1.174412431
69	-1.174462947
88	-1.174465788
127	-1.174468473
130	-1.174468862
134	-1.174468977
139	-1.174469047
141	-1.174469087

ducting such calculations. To that end, we have provided the necessary generalized formulas for analytic first derivatives in the multicenter GG basis. Proposed future efforts would include refinement of this procedure to improve efficiency for large basis-set size. An analytic form for the Hessian would be of important utility should basis set term-coupling exist and would be expected to greatly enhance overall convergence as well. Successful achievement of these goals would significantly contribute to the application of this general methodology to  $n$ -particle systems and systems with higher angular momentum.

#### ACKNOWLEDGMENTS

This study was supported by the National Science Foundation under Grant No. CHE-9300497.

#### References

1. E. A. Hylleraas, Z. Phys. **54**, 347 (1929).
2. H. M. James and A. S. Coolidge, J. Chem. Phys. **1**, 825 (1933).
3. W. Kolos and L. Wolniewicz, J. Chem. Phys. **43**, 2429 (1965).
4. D. M. Fromm and R. N. Hill, Phys. Rev. A **36**, 1013 (1987).
5. F. W. King, Phys. Rev. A **44**, 7108 (1991).
6. S. F. Boys, Proc. R. Soc. Lond. Ser. A **258**, 402 (1960).
7. K. Singer, Proc. R. Soc. Lond. Ser. A **258**, 412 (1960).
8. W. A. Lester, Jr. and M. Krauss, J. Chem. Phys. **41**, 1407 (1964); *Ibid.* **41**, 2990 (1965).
9. P. M. Kozlowski and L. Adamowicz, J. Chem. Phys. **95**, 6681 (1991).
10. P. M. Kozlowski and L. Adamowicz, J. Comput. Chem. **13**, 602 (1992).
11. K. Szalewicz, B. Jeziorski, H. J. Monkhorst, and J. G. Zabolitzky, J. Chem. Phys. **78**, 1420 (1983).
12. P. M. Kozlowski and L. Adamowicz, Phys. Rev. A **48**, 1903 (1993).
13. P. M. Kozlowski and L. Adamowicz, Chem. Rev. **93**, 2007 (1993).
14. J. Komasa and A. J. Thakkar, Mol. Phys. **78**, 1093 (1993).
15. W. Cencek and J. Rychlewski, J. Chem. Phys. **98**, 1253 (1993).
16. J. W. Liu and S. Hagstrom, Phys. Rev. A **48**, 166 (1993).
17. W. Kolos, J. Chem. Phys. **101**, 1330 (1994).
18. M. J. D. Powell, Math. Program. **29**, 297 (1977).
19. R. D. Poshusta, J. Quantum Chem., Quantum Chem. Symp. **13**, 59 (1979).
20. S. A. Alexander, H. J. Monkhorst, and K. Szalewicz, J. Chem. Phys. **85**, 5821 (1986).
21. S. A. Alexander, H. J. Monkhorst, and R. Roeland, J. Chem. Phys. **93**, 4230 (1990).
22. S. Rybak and K. Szalewicz, J. Chem. Phys. **91**, 4479 (1989).
23. P. M. Kozlowski and L. Adamowicz, J. Chem. Phys. **96**, 9013 (1992).
24. D. B. Kinghorn, Int. J. Quantum Chem. (in press).
25. D. B. Kinghorn, Int. J. Quantum Chem. **57**, 141 (1996).
26. J. Rychlewski, W. Cencek, and J. Komasa, Chem. Phys. Lett. **229**, 659 (1994).