Efficient Evaluation of the Matrix Elements of the Coulomb Potential between Plane Waves and Gaussians

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DEDICATED TO THE MEMORY OF MARTIN POLÁŠEK, WHO DIED TRAGICALLY EARLIER THIS YEAR

We present an efficient method for the calculation of matrix elements between two plane waves interacting with a molecular Coulombic field. The molecular charge density is considered a sum of the nuclear point charges and the electronic part developed in products of Gaussian-type functions. The Gaussians may have arbitrary powers of x, y, z before the exponential term. The same method is also applied to the calculation of derivatives of the Coulomb matrix elements with respect to the positions of atomic nuclei. These elements are useful in multichannel treatment of electron–molecule collisions with vibrational excitation of the molecule. Sample calculations of Coulombic matrix elements for the H_2 molecule with Cartesian Gaussian basis set are reported.　ⓒ 2002 Elsevier Science (USA)

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1. INTRODUCTION

The purpose of this paper is to develop a simple and effective algorithm for the evaluation of Coulomb integrals encountered in scattering theories. Recently we published a method [1, 2] for the numerical treatment of electron–molecule scattering problems. The method is based on a numerical solution of the Lippmann–Schwinger integral equation in momentum space. The numerical integration is performed by the Gaussian quadrature. When restricted to the static-exchange approximation, Coulomb and exchange integrals over plane waves are needed. Compared to the Coulomb part, the exchange contribution is a weaker and smoother part of the interaction between the scattering electron and a molecule. On the other hand, evaluation of exchange integrals was in fact the main computational task of our calculations. We devoted therefore much attention to this problem, and thus our effort

resulted in the development [3, 4] of methods for a more efficient evaluation of exchange integrals. When these new methods were combined with the interpolation of exchange integrals from a smaller angular numerical quadrature to a larger quadrature, the evaluation of free–free Coulomb integrals became the most time-consuming step of our calculations. We succeeded in speeding up this step also in a way which is described in this paper. The formulas for free–free Coulomb integrals have been available in the literatute [5, 6] for a long time. Watson and McKoy [7] published them in a form suitable for computer coding. The advantage of our formulas for the free–free Coulomb integrals over those reported by Watson and McKoy [7] is the factorization of terms that are common to all pairs of plane-wave functions from a given basis set and that they can be easily differentiated with respect to the coordinates of atoms in the target.

2. METHOD

The static or Coulombic part of the molecular potential is given by

$$V_s = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}', \tag{1}$$

where $\rho(\mathbf{r})$ is the total charge density of the molecule

$$\rho(\mathbf{r}) = \sum_A Z_A \delta(\mathbf{r} - \mathbf{R}_A) - d_{el}(\mathbf{r}), \tag{2}$$

where Z_A and $\mathbf{R}_A$ are nuclear charge and coordinate, respectively, and $d_{el}(\mathbf{r})$ is the electron density. Our task is to derive an algorithm for the matrix element

$$\langle \mathbf{k}_1 | V_s | \mathbf{k}_2 \rangle = \frac{1}{8\pi^3} \int e^{i\mathbf{K}\cdot\mathbf{r}} V_s(\mathbf{r}) \, d\mathbf{r}, \tag{3}$$

usually referred to as the Coulomb integral. Here $\mathbf{K} = \mathbf{k}_2 - \mathbf{k}_1$. Representing the two-electron operator as a Fourier integral

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} = \frac{1}{2\pi^2} \int \frac{d\mathbf{k}}{k^2} e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')}, \tag{4}$$

the matrix element (3) is written as

$$\langle \mathbf{k}_1 | V_s | \mathbf{k}_2 \rangle = \frac{1}{2\pi^2 K^2} \int \rho(\mathbf{r}) e^{i\mathbf{K}\cdot\mathbf{r}} \, d\mathbf{r}. \tag{5}$$

The term on the right side diverges if $K \to 0$. This fact complicates use of the above formula in scattering calculations. However, as mentioned in [1], for the purpose of solving the Lippmann–Schwinger equation, the forward term may by replaced by

$$\langle \mathbf{k} | V_s | \mathbf{k} \rangle = -\frac{1}{4\pi^2 k^2} \mathbf{k}^T \mathbf{M} \mathbf{k}, \tag{6}$$

where $\mathbf{M}$ is the molecular second moment.

Program packages for molecular structure calculations mostly assume electron density in the form

$$d_{el} = \sum_i \sum_j D_{ij} g_i(\mathbf{r}) g_j(\mathbf{r}), \tag{7}$$

where $g_k(\mathbf{r})$ denotes a Gaussian-type function. We limit ourselves to the Cartesian Gaussians centered at position $\mathbf{A}$

$$g_k(\mathbf{r}) = N_k (x - A_x)^{m_x} (y - A_y)^{m_y} (z - A_z)^{m_z} e^{-a(\mathbf{r}-\mathbf{A})^2}, \tag{8}$$

with the normalisation factor

$$N_k = \left[\left(\frac{\pi}{2a} \right)^{3/2} \frac{(2m_x - 1)!!(2m_y - 1)!!(2m_z - 1)!!}{2^{2(m_x+m_y+m_z)} a^{m_x+m_y+m_z}} \right]^{-1/2}. \tag{9}$$

Conversion of our results to other types such as Hermitian or spherical Gaussians can be made by simple transformation. One of the advantages of using Gaussians in physics and chemistry is that integrals of type (5) can be separated in the form

$$I(\mathbf{A}, \mathbf{B}, i, j, \mathbf{K}) = \int g_i(\mathbf{r} - \mathbf{A}) g_j(\mathbf{r} - \mathbf{B}) e^{i\mathbf{K}\cdot\mathbf{r}} \, d\mathbf{r}$$

$$= N_i N_j e^{-\frac{ab}{a+b}|\mathbf{A}-\mathbf{B}|^2} J_x^{m_x n_x}(i, j) J_y^{m_y n_y}(i, j) J_z^{m_z n_z}(i, j). \tag{10}$$

Now the problem reduces to the evaluation of one-dimensional integrals

$$J_x^{m,n}(i, j) = \int_{-\infty}^{\infty} (x - A_x)^m (x - B_x)^n e^{-\gamma(x-P_x)^2} e^{iK_x x} \, dx, \tag{11}$$

where

$$\gamma = a + b \tag{12}$$

$$\mathbf{P} = \frac{a\mathbf{A} + b\mathbf{B}}{a + b}. \tag{13}$$

The integral (11) can be written in compact form

$$J_x^{m,n}(i, j) = \sum_{k=0}^{m+n} c_k^{m,n}(A_x, B_x, P_x) \Phi_k(\gamma, P_x, K_x), \tag{14}$$

where $\Phi_k(\gamma, P_x, K_x)$ denotes the integral

$$\Phi_k(\gamma, P_x, K_x) = \int_{-\infty}^{+\infty} (x - P_x)^k e^{-\gamma(x-P_x)^2} e^{iK_x x} \, dx. \tag{15}$$

The quantities $c_k^{m,n}(A_x, B_x, P_x)$ and $\Phi_k(\gamma, P_x, K_x)$ are determined by recurrence relations

$$\Phi_{k+2}(\gamma, P_x, K_x) = -\frac{\partial}{\partial \gamma} \Phi_k(\gamma, P_x, K_x) = \frac{iK_x}{2\gamma} \Phi_{k+1}(\gamma, P_x, K_x) + \frac{K-1}{2\gamma} \Phi_k(\gamma, P_x, K_x) \tag{16}$$

and

$$c_k^{m+1,n}(A_x, B_x, P_x) = (P_x - A_x)c_k^{m,n}(A_x, B_x, P_x) + c_{k-1}^{m,n}(A_x, B_x, P_x) \tag{17}$$

$$c_k^{m,n+1}(A_x, B_x, P_x) = (P_x - B_x)c_k^{m,n}(A_x, B_x, P_x) + c_{k-1}^{m,n}(A_x, B_x, P_x). \tag{18}$$

The system of Eqs. (16)–(18) can be treated on a computer as a recursive procedure with boundary conditions

$$\Phi_0(\gamma, P_x, K_x) = \sqrt{\frac{\pi}{\gamma}} e^{i K_x P_x - \frac{K_x^2}{4\gamma}} \tag{19}$$

$$\Phi_1(\gamma, P_x, K_x) = \frac{i K_x}{2\gamma} \Phi_0(\gamma, P_x, K_x) \tag{20}$$

$$c_0^{0,0}(A_x, B_x, P_x) = 1 \tag{21}$$

$$c_0^{1,0}(A_x, B_x, P_x) = P_x - A_x, \quad c_0^{0,1}(A_x, B_x, P_x) = P_x - B_x. \tag{22}$$

The above procedure may also be applied to the calculation of molecular second moments, which can be represented by means of products of integrals (11). For example,

$$\int xy g_i(\mathbf{r}) g_j(\mathbf{r}) \, d\mathbf{r} = N_i N_j e^{-\frac{ab}{a+b}} \left(J_x'^{m_x n_x}(i,j) J_y'^{m_y n_y}(i,j) J_z^{m_z n_z}(i,j) \right. $$
$$+ P_x J_x^{m_x n_x}(i,j) J_y'^{m_y n_y}(i,j) J_z^{m_z n_z}(i,j) + P_y J_x'^{m_x n_x}(i,j) J_y^{m_y n_y}(i,j)$$
$$\left. \times J_z^{m_z n_z}(i,j) + P_x P_y J_x^{m_x n_x}(i,j) J_y^{m_y n_y}(i,j) J_z^{m_z n_z}(i,j) \right) \tag{23}$$

and

$$\int x^2 g_i(\mathbf{r}) g_j(\mathbf{r}) \, d\mathbf{r} = N_a N_b e^{-\frac{ab}{a+b}} \left(J_x''^{m_x n_x}(i,j) J_y^{m_y n_y}(i,j) J_z^{m_z n_z}(i,j) \right.$$
$$+ 2 P_x J_x'^{m_x n_x}(i,j) J_y^{m_y n_y}(i,j) J_z^{m_z n_z}(i,j)$$
$$\left. + P_x^2 J_x^{m_x n_x}(i,j) J_y^{m_y n_y}(i,j) J_z^{m_z n_z}(i,j) \right). \tag{24}$$

The modified integrals (11) are defined as

$$J_x'^{m,n}(i,j) = \sum_{k=0}^{m+n} c_k^{m,n}(A_x, B_x, P_x) \Phi_{k+1}(\gamma, P_x, K_x) \tag{25}$$

and

$$J_x''^{m,n}(i,j) = \sum_{k=0}^{m+n} c_k^{m,n}(A_x, B_x, P_x) \Phi_{k+2}(\gamma, P_x, K_x). \tag{26}$$

3. DERIVATIVES OF COULOMBIC INTEGRALS

Calculations of molecular processes involving small displacements of nuclear positions are usually made with the help of first- and second-order Taylor expansions of operators describing the system. A well-known example is the analytic method [10] for the evaluation of molecular force constants within of Hartree–Fock approximation. The method uses

expansion of molecular orbitals under the influence of displacements of nuclei with respect to their equilibrium positions so that the new density matrix in Eq. (7) can be written as

$$P_{\alpha\beta} = \sum_{i \in occ} \sum_k \sum_l U_{ik}^* c_{\alpha k}^* U_{il} c_{\beta l}. \tag{27}$$

Here the quantities $c_{\alpha k}$ are expansion coefficients of molecular orbitals in the Gaussian basis set. Greek symbols are indices for Gaussians; Latin letters count for molecular orbitals. The matrix U contains all information about changing the molecular orbitals with respect to external perturbation [8, 9]. When restricted to the first-order perturbation theory, the elements of the matrix U can be written as

$$U_{ik}(Q) = \delta_{ik} - u_{ik} Q, \tag{28}$$

where Q stands for a perturbational parameter. The coefficients u_{ik} are usually called coupled perturbed Hartree–Fock (CPHF) coefficients and they can be obtained by a set of linear CPHF equations. The formulas suitable for computer coding were published by Pople and collaborators [10].

In electron–molecule scattering, displacement of atomic nuclei appears in collision theories accompanied by vibrational excitation of the molecular target. The multichannel treatment of electron–molecule scattering accompanied by vibrational excitation requires knowledge of matrix elements of the type

$$\langle \Psi_1(\mathbf{r}, \mathbf{R}) | V_s(\mathbf{r}, \mathbf{R}) | \Psi_2(\mathbf{r}, \mathbf{R}) \rangle. \tag{29}$$

The static potential now depends on both electronic ($\mathbf{r}$) and nuclear ($\mathbf{R}$) coordinates. In adiabatic approximation the element (29) reduces to

$$\langle \mathbf{k}_1 \chi_i(Q) | V_s(\mathbf{r}, \mathbf{R}) | \mathbf{k}_2 \chi_j(Q) \rangle. \tag{30}$$

Here χ_n is the wavefunction of the nth vibrational state; Q represents a normal coordinate corresponding to this particular state. Expanding the static potential into the Taylor series up to the first-order and using well-known properties of eigenfunctions of the harmonic oscillator we get

$$\begin{aligned} \langle \mathbf{k}_1 \chi_i(Q) | V_s(\mathbf{r}, \mathbf{R}) | \mathbf{k}_2 \chi_j(Q) \rangle \approx & \langle \mathbf{k}_1 | V_s(\mathbf{r}, \mathbf{R}) | \mathbf{k}_2 \rangle \delta_{ij} \\ & + \frac{1}{\sqrt{2}} \frac{\partial \langle \mathbf{k}_1 | V_s(\mathbf{r}, \mathbf{R}) | \mathbf{k}_2 \rangle}{\partial Q} (\delta_{i-1,j} + \delta_{i+1,j}). \end{aligned} \tag{31}$$

Evaluation of derivatives of the static potential now reduces to the derivation of the quantity (10) with respect to nuclear coordinates

$$\frac{\partial I(\mathbf{A}, \mathbf{B}, i, j, \mathbf{K})}{\partial \mathbf{C}}. \tag{32}$$

The expression (32) is zero if $\mathbf{C} \neq \mathbf{A}$ and $\mathbf{C} \neq \mathbf{B}$. If both Gaussians are centered on the same

atom, the evaluation is also very easy. Let us shift the position of nucleus $\mathbf{A}$

$$I(\mathbf{A} + \mathbf{\Delta}, \mathbf{A} + \mathbf{\Delta}, i, j, \mathbf{K}) = \int g_a(\mathbf{r} - \mathbf{A} - \mathbf{\Delta}) g_b(\mathbf{r} - \mathbf{A} - \mathbf{\Delta}) e^{i\mathbf{K} \cdot \mathbf{r}} \, d\mathbf{r}$$

$$= e^{i\mathbf{K} \cdot \mathbf{\Delta}} I(\mathbf{A}, \mathbf{A}, i, j, \mathbf{K}). \tag{33}$$

Differentiation with respect to $\mathbf{\Delta}$ yields

$$\frac{\partial I(\mathbf{A}, \mathbf{A}, i, j, \mathbf{K})}{\partial \mathbf{A}} = i\mathbf{K} I(\mathbf{A}, \mathbf{A}, i, j, \mathbf{K}). \tag{34}$$

In a general case we may obtain the derivatives directly from the formulas introduced in Section 2:

$$\frac{\partial I(\mathbf{A}, \mathbf{B}, i, j, \mathbf{K})}{\partial A_x}$$

$$= N_a N_b e^{-\frac{ab}{a+b}|\mathbf{A} - \mathbf{B}|^2} \left[\frac{\partial J_x^{m_x n_x}(i, j)}{\partial A_x} J_y^{m_y n_y}(i, j) J_z^{m_z n_z}(i, j) - \frac{2ab}{a+b} A_x I(\mathbf{A}, \mathbf{B}, i, j, \mathbf{K}) \right]. \tag{35}$$

In the following expressions we omit the subscripts indicating a particular Cartesian coordinate:

$$\frac{\partial J_x^{m_x n_x}(i, j)}{\partial A_x} = J^{mn}(i, j)_{(A)}$$

$$= \sum_{k=0}^{m+n} c_{k(A)}^{m,n}(A, B, P) \Phi_k(\gamma, P, K) + \sum_{k=0}^{m+n} c_k^{m,n}(A, B, P) \Phi_{k(A)}(\gamma, P, K). \tag{36}$$

Recurrence relations for all derivatives in the last equation can be obtained directly from Eqs. (16)–(22):

$$\Phi_{k+2(A)}(\gamma, P, K) = \frac{iK}{2\gamma} \Phi_{k+1(A)}(\gamma, P, K) + \frac{k-1}{2\gamma} \Phi_{k-2(A)}(\gamma, P, K) \tag{37}$$

and

$$C_{k(A)}^{m+1,n}(A, B, P) = (P - A) c_{k(A)}^{m,n}(A, B, P) + c_{k-1(A)}^{m,n}(A, B, P) + \frac{\beta}{\gamma} c_k^{m,n}(A, B, P) \tag{38}$$

$$C_{k(A)}^{m,n+1}(A, B, P) = (P - B) c_{k(A)}^{m,n}(A, B, P) + c_{k-1(A)}^{m,n}(A, B, P) + \frac{\alpha}{\gamma} c_k^{m,n}(A, B, P) \tag{39}$$

$$\Phi_{0(A)}(\gamma, P, K) = \frac{iK}{\gamma} \Phi_0(\gamma, P, K) \tag{40}$$

$$\Phi_{1(A)}(\gamma, P, K) = \frac{iK}{2\gamma} \Phi_{0(A)}(\gamma, P, K) \tag{41}$$

$$c_{0(A)}^{0,0}(A, B, P) = 0. \tag{42}$$

$$c_{0(A)}^{1,0}(A, B, P) = -\frac{\beta}{\gamma}, \quad c_{0(A)}^{0,1}(A, B, P) = \frac{\alpha}{\gamma}. \tag{43}$$

TABLE I
Gaussian Basis Set Used for the Calculation

$m_x + m_y + m_z$	Exponent	Contraction coefficient
0	33.87000000	0.00606800
	5.09500000	0.04530800
	1.15900000	0.20282200
0	0.32580000	1.00000000
0	0.10270000	1.00000000
1	1.40700000	1.00000000
1	0.38800000	1.00000000
2	1.05700000	1.00000000

The derivatives of the density matrix needed in Eq. (7) can be easily obtained by use of standard electronic structure theory program packages.

4. NOTES ON COMPUTATIONAL PROCEDURES AND BENCHMARK RESULTS

In the context of electron– and positron–molecule collisions, the method presented here has two main advantages. First, it can be applied to Gaussian basis sets with the arbitrary power of the preexponential function. The second advantage follows from Eqs. (17), (18) and (21), (22). If the wavefunction of the scattered electron is represented in momentum space, one usually needs a large number of quadrature nodes to integrate the Lippmann–Schwinger equation with sufficient accuracy. Typically, it is considerably larger than the number of Gaussians necessary for accurate representation of electron density. It is clear by inspection of the set of Eqs. (16)–(18) that computationally the most demanding step is represented by the pair of recurrence relations (17) and (18). The coefficients $c_{k(A)}^{m,n}(A, B, P)$ do not depend on $\mathbf{K}$, so it is advantageous to evaluate them first, keep them in memory, and use them in all the steps when $\mathbf{K}$ is changed. The same holds for the calculation of derivatives of Coulombic integrals.

To present benchmark results of our algorithm, we calculated Coulomb integrals and their derivatives for electron–H_2 scattering. The Dunning's cc-pVTZ Gaussian basis set [11] was used for the generation of molecular density. This basis set can be denoted as $[3s2p1d]$. The exponents and contraction coefficients are listed in Table I. The pair of $\mathbf{k}_1$ and $\mathbf{k}_2$ vectors in Eq. (3) was fixed in a line and the second vector was scanned from five different positions. The Cartesian coordinates (in atomic units) of atomic nuclei were fixed at $(0,0,-1)$ and $(0,0,1)$, respectively. The last column of Table II contains derivatives of Coulombic integrals with respect to the Z-position of the first atom. The results are

TABLE II
Coulomb Integrals for e–H_2 Scattering

K_x	K_y	K_z	$\langle \mathbf{k}_1 \vert V_s \vert \mathbf{k}_2 \rangle$	$\frac{\partial}{\partial Z_1} \langle \mathbf{k}_1 \vert V_s \vert \mathbf{k}_2 \rangle$
0.000000	0.000000	0.000000	$(-0.5947965E-01, 0.0000000E+00)$	$(-0.2121398E-03, 0.0000000E+00)$
0.017101	0.029620	0.093969	$(-0.5893961E-01, -0.2763876E-14)$	$(-0.6691569E-03, -0.2769256E-02)$
0.034202	0.059240	0.187939	$(-0.5734116E-01, -0.1207362E-14)$	$(-0.2011707E-02, -0.5388307E-02)$
0.051303	0.088859	0.281908	$(-0.5475436E-01, -0.5218139E-15)$	$(-0.4157089E-02, -0.7717840E-02)$
0.068404	0.118479	0.375877	$(-0.5128719E-01, -0.3371799E-15)$	$(-0.6976542E-02, -0.9638838E-02)$
0.085505	0.148099	0.469846	$(-0.4707853E-01, -0.1822238E-15)$	$(-0.1030740E-01, -0.1105984E-01)$

summarized in Table II. Since the values of the integrals (last two columns) depend only on the difference vector $\mathbf{K} = \mathbf{k}_1 - \mathbf{k}_2$, Cartesian coordinates of this vector were used as independent variables.

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