Note on the Generation of Gaussian Bases for Pseudopotential Calculations

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ABSTRACT

We present a technique to generate Cartesian Gaussian bases for electronic configuration and cross-section calculations on molecules. The technique is specially useful for pseudopotential work, when the bases cannot be tabulated because they depend on the specific choice of the pseudopotential. © 1996 John Wiley & Sons, Inc.

Introduction

The advantages of pseudopotentials (or effective potentials) over all-electron calculations are twofold. First, with pseudopotentials, one avoids calculating core electrons which have little importance in chemistry. This reduction in the computational work is enormous when dealing with heavy atoms. Second, if one uses the so-called norm-conserving pseudopotentials [1]–[6], which are specially smooth functions (or integral operators) with no singularity at the nucleus, the resulting one-electron wave functions are also very smooth, with no nodes for the occupied valence states, and can be expanded in very small sets of Gaussian functions (three or four only). While for all-electron work there are complete tabulations of Gaussian bases [7]–[10], for pseudopotentials no such tables are expected because there is no “best” pseudopotential and no unique way to define it. Thus, each pseudopotential user is entitled to personal preferences but must pay the price of generating his or her own Gaussian bases [11].

In this note we show a new and effective way to generate Gaussian bases for pseudopotential work. We mention that our motivation was the calculation of electron-molecule scattering cross sections with pseudopotentials [12]. In this process we developed a Gaussian basis generation scheme of very broad applicability.

The bases are generated in two steps:

1. We calculate the atom within the local-density approximation (LDA), using a standard approximation for exchange correlation, for example, that of Ref. [13] and the pseudopotential that is going to be used in the molecular calculation. The output of such calculations is the set of one-
electron eigenfunctions numerically defined in a radial net. Of course, the code for the atomic calculations is not necessarily LDA based, but a restricted Hartree–Fock (RHF) code serves the purpose as well, the transferability of pseudopotentials and wave functions from the LDA and HF frameworks being a well-known fact.

2. Once the eigenfunctions are tabulated in a radial net, we proceeded with its matching by a series of Cartesian Gaussians. Our first attempt was to use a least-square fit of the LDA eigenfunction $u(r)$ by a series of Gaussians $\tilde{u}(r)$ [2]. That is,

$$Q[\tilde{u}] = \int r^2[\tilde{u}(r) - u(r)]^2 dr = \text{minimum},$$

where $\tilde{u}(r)$ is the series of Cartesian Gaussians:

$$\tilde{u}(r) = \sum_i D_i r^i \exp(-\gamma_i r^2).$$

In some instances (when the number of Gaussians was very small, in the order of 2 or 3), the least-square process lead to degenerate Gaussians (Gaussians with the same exponent $\gamma_i$) and a poor fit. The least-square process tries to match $\tilde{u}(r)$ to $u(r)$, while what is energetically important is not the wave function itself but its Laplacian. In other words, $\tilde{u}(r)$ and $u(r)$ may be very close, but, after two derivations, their difference may be substantial. What we tried next, with success, was to use a variational principle equivalent to the Poisson equation, imported from simple electrostatic theory.

Consider the following functional [14]

$$F[\tilde{S}] = \int d^3 r (\nabla \tilde{S})^2 + 2 \int d^3 r V(r) \tilde{S}(r),$$

whose minimum happens when

$$\nabla^2 \tilde{S} = V(r),$$

which is the Poisson equation. Let

$$U(r) = u(r) Y_{lm}(\hat{r})$$

be the exact one-electron wave function where $u(r)$ is defined in the radial net; $u(r)$ will be matched by the series of Gaussians [Eq. (2)] and the wavefunction $U(r)$ will be matched by

$$\tilde{U}(r) = \tilde{u}(r) Y_{lm}(\hat{r}).$$

Then we set

$$V(r) = \nabla^2 U + K U(r),$$

where $K$ is a constant that may be used to control the matching. To make the matching result from the minimization of the functional, it is then sufficient to set

$$\nabla^2 \tilde{S} = \nabla^2 \tilde{U} + K \tilde{U}(r)$$

with

$$\tilde{S}(r) = \tilde{s}(r) Y_{lm}(\hat{r})$$

in which case, Eqs. (4), (7), and (8) lead to

$$\nabla^2 \tilde{U} + K \tilde{U}(r) = \nabla^2 U + K U(r).$$

Therefore, if $K = 0$, the functional Eq. (3) is minimized when the Laplacian of the Gaussian series $\tilde{U}(r)$ coincides with the Laplacian of the LDA eigenfunction $U(r)$. If $K = \infty$, the minimization is attained when $\tilde{U} = U$. Other values of $K$ determine other matching types. For sufficiently long Gaussian series, the value of $K$ does not matter.

Equation (8) is solved to give

$$\tilde{S}(r) = \sum_i D_i r^i \exp(-\gamma_i r^2)$$

$$- \frac{1}{r^{i+1}} \sum_i \frac{K D_i}{2 \gamma_i} \int_0^r r'^{2i} \exp(-\gamma_i r'^2) dr,$$

and the final expression for the functional becomes

$$F = \sum_{i,l} D_i \langle i \mid \hat{p} D_j \rangle + 2 \sum_i D_i \langle i \mid \tilde{u} \rangle,$$

where the brackets are

$$\langle i \mid j \rangle = \frac{\pi^{1/2}}{2} \frac{(2l + 1)!!}{(2l + 1)!!} \left[ \frac{K^2}{4 \gamma_i \gamma_j} - \frac{(2l + 1)K}{\gamma_i + \gamma_j} + \frac{(2l + 1)(2l + 3)\gamma_i \gamma_j}{(\gamma_i + \gamma_j)^2} \right].$$

$$\langle i \mid \tilde{w} \rangle = \int_0^\infty u(r) \left[ -2 \gamma_i (2l + 3) r^{i+2} + 4 \gamma_i^2 r^{i+4} + 2 K r^{i+2} \right] \exp(-\gamma_i r^2) dr$$

$$- \frac{K^2}{2 \gamma_i} \int_0^\infty r^{2i} \exp(-\gamma_i r^2) dr \int_0^\infty \frac{ru(r)}{r^i} dr.$$
The minimization of the functional with respect to the coefficients $D_i$ is, of course, trivial. The brackets, though corresponding to Laplacians, require no numerical derivations but only integrations which are easy and precise. The minimization with respect to the exponents $\gamma_i$ requires a better care, and we found that the method proposed in Ref. [15] is adequate.

From the expressions of the brackets above, one sees that the case of $K = \infty$ (fitting $\mathcal{U}(r)$ to $\mathcal{U}(r)$, not $\nabla^2 \mathcal{U}$ to $\nabla^2 \mathcal{U}$) corresponds to a least-square fitting of the series

$$\sum_i \frac{D_i}{2\gamma_i} r^i \exp(-\gamma_i r^2) = r^i \int_r^\infty \frac{tu(t)}{t^i} dt$$

to the following transform of $u(r)$

$$r^i \int_r^\infty \frac{tu(t)}{t^i} dt.$$ 

Further, the derivatives of Eqs. (13) and (14) with respect to $K$, taken at $K = 0$, are exactly the equations obtained from the minimization of least-square functional [Eq. (1)]. Thus, the minimization of the Poisson functional [Eq. (3)] may lead to assorted fitting procedures. We found that, for small number of Gaussians, the best fitting happened at small values of $K$, around $K = 0$.

### Test Case Calculations

Our double recipe for Gaussian bases generation [(1) LDA calculation of the atomic wave functions and (2) matching the Gaussian series to the LDA wave functions by means of the Poisson functional, Eq. (3)] is intended to be of wide applicability. We have been using the recipe for many atoms (C, F, Cl, Br, I, Si, [16] Ge, Sn, Pb, O, H, S, Li, Na, Ar) in connection with molecular cross-section calculations. We require that the basis is such that the one-electron energy eigenvalues are off the true LDA eigenvalues by no more than 0.001 Ryd. Usually, the resulting basis has 3 to 4 Gaussian exponents for s and 3 exponents for p.

In the case of Na, because we needed highly excited states in our study of the Na$_2$ molecule, we found an s-basis with 7 exponents and a p-basis with 5 exponents able to reproduce the one-electron energy eigenvalues with the precision shown in Table I. For the reader unaware of pseudopotential techniques, we mention that the wave function 3s has 0 nodes, 4s has 1 node, etc., and 3p has 0 nodes, 4p has 1 node, etc.

In the case of Ar we made pseudopotential Hartree–Fock total energy calculations. The pseudopotential used was that of Ref. [3]. First, we used a standard all-electron (10s, 6p) basis [10] to obtain a total energy of $-41.766$ Ryd. Then we used our recipe to generate a (4s4p) basis with which we obtained the lower energy $-41.839$ Ryd. By increasing this basis up to (10s10p) we estimate the Hartree–Fock limit to be $-41.841$ Ryd. Finally, to convince the reader not familiar with pseudopotential techniques of the broad applicability of our recipe, we also used it to generate bases for all-electron calculations. Thus we generated a (11s7p) basis and obtained a Hartree–Fock total energy of $-1053.496$ Ryd which is lower than the value for the standard (10s, 6p) basis ($-1053.346$ Ryd).

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### References


### TABLE I

Energy eigenvalues (Ryd) for Na and a (7s, 5p) basis.

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<th>Basis</th>
<th>Exact</th>
<th>(7s, 5p) basis</th>
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<td>3s</td>
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