A Method for Selection and Use of Numerical Integration Points for Molecules with Cylindrical Symmetry*

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Boys and Handy [1] have discussed the solution of the bivariational equations with restricted numerical integration. One of the weaknesses of the method was that in the numerical summations over points, some points arose with $r_{ij}=0$ and non-zero weights. This makes the method quite impractical for the Schrodinger Hamiltonian (because of the singularity at $r_{ij}=0$), and it cannot be advantageous for the transcorrelated Hamiltonian $C^{-1}HC$ because there will be some discontinuous higher derivatives at $r_{ij}=0$. Here it is shown how the symmetry of cylindrically symmetric molecules can be used to eliminate such points, without losing any of the advantages of the overall method, such as the convergence of the eigensolutions. It is also shown how the primary numerical integration points (z_i, r_i) may be chosen in any calculation such that each is associated with an equal amount of one-electron density. The choice of the angular coordinates are governed by the removal of the $r_{ij}=0$ points and maintaining the natural orthogonality between orbitals of different symmetry types. The method has been programmed and found to be practical, although no new molecular calculations have yet been performed. It is to be hoped that these points will give a basis for new transcorrelated calculations on diatomic molecules.

Key words: Transcorrelated method – Numerical integration

1. Removal of $R_{ij}=0$ Contributions

Boys and Handy [1] have discussed the solution of the bivariational equations with restricted numerical integration

$$\langle \Psi_r Q | H - W | \sum_s Y_s \Phi_s \rangle = 0 \tag{1}$$

Here Ψ_r and Φ_s denote Slater determinants and H may denote either the Schrodinger Hamiltonian H_s or the Transcorrelated Hamiltonian $C^{-1}H_sC$, and W is the associated eigenvalue. Q denotes the restricted numerical integration operator

$$Q = \sum_i^M h_i \delta(r_1, R_i) \sum_j^M h_j \delta(r_2, R_j) \dots \sum_u^M h_u \delta(r_N, R_u) \tag{2}$$

where (h_i, R_i) are a set of M weights and points in 3 dimensions, and N is the number of electrons.

The above authors have underlined the advantages of working with Eq. (1): firstly, the error in W is proportional to μ, the least squares error of the basis set Φ_s to the true eigenfunction, whatever the functions Ψ_r and Q; secondly,

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a Slater determinant Projective Reduction theorem can be derived for the evaluation of the matrix elements, on a parallel with the standard theorem for the accurate determination of these elements (when $Q=1$) through 6-dimensional integrals. Thus for a two electron operator F, $\langle \Psi_r Q | \overset{\pm}{\underset{ij}{\sum}} F_{ij} | \Phi_s \rangle$ is a linear combination of sums S of the form

$$S = \sum_i^M h_i \sum_j^M h_j \psi_a^*(R_i) \, \psi_b^*(R_j) \, F(R_i, R_j) \, \varphi_c(R_i) \, \varphi_d(R_j) \tag{3}$$

where ψ and φ are one electron orbitals occurring in Ψ_r and Φ_s, and satisfying

$$\sum_i h_i \psi_a^*(R_i) \, \varphi_c(R_i) = \delta_{ac} \tag{4}$$

This procedure was successfully used in calculations with the transcorrelated method on LiH.

In the sum S, it will be noticed that i equals j M times and so $R_{ij}=0$ occurs M times with non zero weights h_i^2, thus making the method particularly unsuitable for operators which have singularities or discontinuities at $r_{ij}=0$. It is therefore impossible to work with H_s, because of r_{ij}^{-1}, and $C^{-1}H_sC$ may give difficulty because there are certainly discontinuities in higher derivatives at $r_{ij}=0$. This is particularly relevant in the present circumstances when the proportion $(1/M)$ of these points to the total points is quite significant, M being small (say 100).

Here it is shown how the symmetry of cylindrically symmetric molecules can be used to remove these undesirable points $R_i = R_j$, through a slight redefinition of Q, the above mentioned advantages still holding true. Essentially the method depends upon the fact that if

$$R_i = (z_i, r_i, \theta_i) \text{ and } R_i^k = \left(z_i, r_i, \theta_i + k\frac{2\pi}{N}\right), \, k = 1, 2, \dots N \tag{5}$$

then whenever (4) holds, so also does

$$\sum_i h_i \psi_a^*(R_i^k) \, \varphi_c(R_i^k) = \delta_{ac} \tag{6}$$

because of the symmetry of the orbitals ψ and φ around the z axis. If the operator Q is therefore replaced by the (symmetric) operator

$$Q = \frac{1}{N!} \sum_k^{N!} P_k \left[\sum_i^M h_i \delta(r_1, R_i^{k_1}) \sum_j^M h_j \delta(r_2, R_j^{k_2}) \sum_u^M h_u \delta(r_N, R_u^{k_N}) \right] \tag{7}$$

where P_k runs over all permutations k of $1, 2, 3 \dots N$, then a Slater determinant Projective Reduction theorem can still be derived, because its derivation depends upon the use of the orthogonality conditions Eq. (6). In this case it appears that S takes the form

$$S = N^{-1}(N-1)^{-1} \sum_{\lambda \neq \mu}^N \sum_i^M h_i \sum_j^M h_j \psi_a^*(R_i^\lambda) \, \psi_b^*(R_j^\mu) \, F(R_i^\lambda, R_j^\mu) \, \varphi_c(R_i^\lambda) \, \varphi_d(R_j^\mu) \tag{8}$$

where it is immediately noticed that no points ever arise with $R_{ij}=0$.

2. Further Substantial Reductions through Symmetry

The cylindrical symmetry can be further used to simplify S. [For expediency, it is assumed here that the orbitals are only of σ type and that F is a function of z, r and r_{ij}]. It is certainly possible to put all the original points on $\theta = 0$, that is $\theta_i = 0$, — Eq. (4) will still hold for σ type orbitals, (for higher symmetry types this is not so, but it is simply corrected by associating with each (z_i, r_i) a certain number of θ points equally spaced around the z axis). Furthermore, for each term in S, it is always possible to rotate the θ axis such that all the R_i points lie on $\theta = 0$, without changing its value, again because of the symmetry. These further arguments give S in the form

$$S = N^{-1}(N-1)^{-1} \sum_{\lambda \neq \mu}^{N} \sum_{ij}^{M} h_i h_j \psi_a^*(R_i^0)\, \psi_b^*(R_j^{\mu-\lambda})\, F(R_i^0, R_j^{\mu-\lambda})\, \varphi_c(R_i^0)\, \varphi_d(R_j^{\mu-\lambda}) \qquad (9)$$

where

$$R_i^0 = (z_i, r_i, 0), \quad R_j^{\mu-\lambda} = \left(z_j, r_j, (\mu-\lambda)\frac{2\pi}{N}\right)$$

The operator F will have different values for different values of $\left[(\mu-\lambda)\dfrac{2\pi}{N}\right] \bmod(\pi)$,

so in effect S is a sum of pM^2 quantities, where p is the number of these distinct values. The method is simply extended, as indicated above, to the case when ψ and φ are of higher symmetry types, m_1 and m_2 say, where the relation (4) takes the form

$$\sum_i h_i \psi_a^{m_1}(R_i)\, \varphi_c^{m_2}(R_i) = \delta_{ac}\delta_{m_1 m_2} \qquad (10)$$

For a calculation on HF involving σ, π, δ occupied and excited orbitals, which uses all the above procedures, thus maintaining the advantages of the restricted integration bivariational method Eq. (1), yet has no $R_{ij} = 0$ points and also obeys Eq. (10), S is a sum of $14 M^2$ finite quantities. [Part of the theory used here will be given in detail in a forthcoming publication [2]].

3. Selection of the M Basic Points R_i^0

It will be assumed for the molecules under consideration that an approximate one electron density function $\varrho(z, r)$ is known, from an SCF calculation or otherwise. The idea here is to divide the 2 dimensional space (z, r) into regions such that each point is associated with an equal amount of electron density. Such a method can be described as follows:

$$\text{Let } f(z) = \int_0^\infty 2\pi r\varrho(z, r)\, dr \quad \text{and} \quad A = \int_{-\infty}^\infty f(z)\, dz \qquad (11)$$

First divide the z axis as follows by choosing $\bar{z}_i$ such that

$$\int_{-\infty}^{\bar{z}_i} f(z)\, dz = (i/L)\, A \quad \text{and} \quad z_i = 1/2\,(\bar{z}_i + \bar{z}_{i-1}) \qquad (12)$$

where $i = 1, 2, \ldots L$, and $L \simeq M^{\frac{1}{2}}$, M being the total number of points required. For each z_i point now determined, the values r_i^j associated with it are similarly selected. Let

$$\int_\infty^{\bar{r}_i^j} 2\pi r\varrho(z_i, r)\, dr = (j/L)\, f(z_i) \quad \text{and} \quad r_i^j = \tfrac{1}{2}\,(\bar{r}_i^j + \bar{r}_i^{j-1}) \qquad (13)$$

for $j = 1, 2, \ldots L$.

As the problem here is only 2 dimensional, all the integrals in the above expressions can be accurately evaluated numerically, using a sufficiently large number of points. Thus in practice $\pm \infty$, $\bar{z}_0$ and $\bar{r}_i^0$ are each replaced by some suitably large value. The $L^2 (\simeq M)$ points (z_i, r_i^j) selected by this procedure will each have equal weight, the 1-electron density space having been divided into L^2 equal areas. In a typical transcorrelated calculation on HF, it is anticipated that $M \simeq 144$, $L \simeq 12$.

4. Conclusion

The above procedures have been programmed for diatomic molecules, and have been found entirely practical. The increase in the number of 6 dimensional points from M^2 to pM^2 does not increase the time factor by p, because of many simplifying details — and in any case, this factor is surely warranted because of the removal of the $R_{ij} = 0$ points.

References

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