

A Modified Electronic Population Analysis for Transition-Metal Complexes

J. OAKLEY NOELL*

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A modification to the Mulliken electronic population analysis designed primarily for use on transition-metal systems is presented. All terms arising from the metal basis functions including diagonal terms are repartitioned between the metal and the ligands. This reapportionment is an attempt to reflect more accurately the actual electron density in well-defined areas of space, which characterize the metal and the ligand. This modified analysis appears to yield more reasonable charge assignments than a conventional Mulliken analysis. The cost of the analysis is negligible in comparison with that of calculating the wave function.

I. Introduction

From the advent of LCAO-MO calculations, efforts have been made toward facile intuitive analysis of electronic populations. The most commonly deployed technique is that due to Mulliken.¹ The concepts of net, gross, and bond overlap populations have proven to be most useful parameters in discussing the qualitative characteristics of a wave function. Within the Mulliken analysis the charge assigned to an atom may be written as

$$Q_A = \sum_i^{\text{occ}} f_i \sum_{\mu \in A} \sum_{\nu} C_{\mu i} C_{\nu i} S_{\mu\nu} \quad (1)$$

where f_i is the occupation number of orbital i , μ and ν are indices of the atomic basis functions, the first sum ranging only over those centered on atom A, $C_{\mu i}$ is the coefficient of basis function μ in orbital i , and $S_{\mu\nu}$ is the overlap integral between the two basis functions. The one facet of a Mulliken analysis that has, over the years, attracted the most attention is the equal partitioning of the bond overlap populations; i.e., the assignment to each of the basic functions μ and ν a population of $C_{\mu i} C_{\nu i} S_{\mu\nu}$ regardless of what the relative magnitude of the coefficients might be. This dilemma has led to numerous redefinitions of atomic populations.²⁻⁸ The most straightforward solution is, of course, to work in an orthogonal basis. The transformation defined by Löwdin is the most useful in this regard.² Other workers have devised weighting schemes for partitioning of the overlap population while still working in a nonorthogonal basis.⁴ The salient feature of all analyses whose spirit is that of Mulliken is that the net populations, i.e., those arising from $C_{\mu i}^2$, are always ascribed to the atom about which that basis function is centered. This is a very reasonable assumption so long as basis functions on one center are not sufficiently diffuse that appreciable density arising from these functions ought more appropriately to be assigned to another atom. For atoms of the first two rows this has not been a severe problem.

With the advent of calculations on transition-metal systems, it has become evident that such a problem is indeed encountered. A proper description of the valence s and p shells of a transition-metal atom requires very diffuse basis functions.^{9,10} As is evident from the plot of the radial density for the valence orbitals of atomic Pt (Figure 1), these functions extend far beyond the covalent radius of the metal. In view of this spatial extent, it is not surprising that their partial occupation in molecular systems yields wave functions not easily interpretable with use of a conventional Mulliken analysis; the metal atom typically appropriates more electrons than intuition can abide. This often leads to a net negative charge on the metal, and the literature is replete with examples of such analyses.¹¹

One tactic, which avoids these difficulties, is simply not to include functions appropriate for the diffuse atomic s and p functions in molecular calculations, assuming that they are not formally occupied in most oxidation states of the molecule and that a tighter, more localized basis will more adequately treat rehybridization effects.^{10,12} This does result in intuitively reasonable population analyses but only at the expense of virtually precluding valence s and p participation in the wave function.¹² This does not seem to be the appropriate solution since the diffuse functions have made significant contributions in calculations in which they have been included.¹¹

The strategy of the present report is to devise a relatively simple modification of the Mulliken population analysis that yields more useful interpretations of wave functions for transition-metal systems while still maintaining the computational ease of the conventional analysis. This latter criterion precludes the use of very time-consuming techniques for population analyses such as three-dimensional quadratures. The analysis formulated in the next section satisfies these criteria and shows promise of being very generally useful for transition-metal systems. In its present formulation, the analysis is applicable only to systems with a single transition-metal atom. Extension to polynuclear transition-metal species should be possible.

In this paper we present only sufficient results to illustrate key points regarding the technique. In the work that follows¹³ on oxidative additions to Pt(0), additional calculations are presented illustrating the interpretive advantages to the modifications presented.

II. Formulation of the Method

The key to the method is the conceptual division of space into the units illustrated in Figure 2 for a square-planar system. A central sphere with radius equal to the covalent radius of

- (1) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833, 1841, 2338, 2743, 3428 (1955).
- (2) P.-O. Löwdin, *J. Chem. Phys.*, **18**, 365 (1950); **21**, 374 (1953).
- (3) E. R. Davidson, *J. Chem. Phys.*, **46**, 3320 (1967).
- (4) R. E. Christofferson, *Chem. Phys. Lett.*, **8**, 4 (1971).
- (5) R. McWeeny, *J. Chem. Phys.*, **19**, 1614 (1951), **20**, 920 (1952).
- (6) M. Pollack and R. Rein, *J. Chem. Phys.*, **47**, 2045 (1967).
- (7) L. Ch. Cusachs and P. Politzer, *Chem. Phys. Lett.*, **1**, 529 (1968); **2**, 1 (1968).
- (8) R. Daudel et al., *C. R. Hebd. Seances Acad. Sci.*, **233**, 1608 (1951); **234**, 2198 (1952); *J. Chem. Phys.*, **49**, 545 (1952).
- (9) A. J. H. Wachters, *J. Chem. Phys.*, **52**, 1033 (1970).
- (10) B. Roos, A. Veillard, and G. Vinot, *Theor. Chim. Acta*, **20**, 1 (1971).
- (11) Cf. the following: C. S. Ewig, R. Osman, and J. R. Van Wazer, *J. Am. Chem. Soc.*, **100**, 5017 (1978); P. J. Hay, *ibid.*, **100**, 2411 (1978); I. H. Hillier and John Kendrick, *Inorg. Chem.*, **15**, 520 (1976); M. F. Guest, I. H. Hillier, B. R. Higginson, and D. R. Lloyd, *Mol. Phys.*, **29**, 113 (1975).
- (12) A. Veillard and J. Demuynck, "Applications of Electronic Structure Theory", H. F. Schaefer III, Ed., Plenum Press, New York, 1977, p 187.
- (13) J. O. Noell and P. J. Hay, *Inorg. Chem.*, following paper in this issue.

* Address for correspondence: Division 8343, Sandia National Laboratory, Livermore, CA 94550.

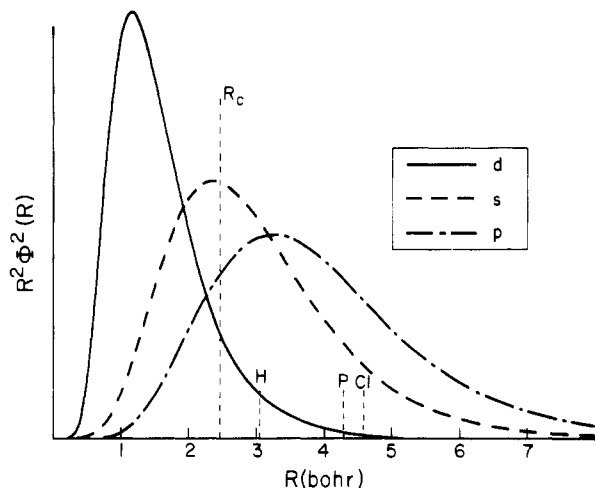


Figure 1. Radial density of the valence s, p, and d orbitals of the Pt atom. The s and d densities are for the 3D (d^9s) state of the atom; the p orbital is from the 5G (d^8sp) atomic state. R_c denotes the covalent radius of the metal (2.46 bohr). The demarcations respectively labeled as H, Cl, and P characterize the approximate metal–ligand bond length.

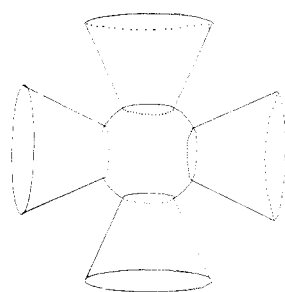


Figure 2. Partitioning of space for a four-coordinate, square-planar system. The central sphere is of radius R_c ; density inside this sphere is apportioned to the metal. For each ligand a cone (30° angles of revolution shown here) is defined within which the density is ascribed to that ligand. All electrons in the interstitial region are defined as belonging to the metal.

the metal defines the space in which is assigned density to the metal atom. The fraction of space whose density will be assigned to a given ligand is defined as the cone of revolution (excluding the region of overlap with the metal's sphere), whose axis is defined by the metal–ligand bond. It is not critical that the cones be tangent to one another, but they must not overlap. It ought to be noted that even with six octahedrally displaced tangent cones, the entire space is not occupied. Any density in a space not defined by one of the ligand cones is assigned to the metal.

There are to ambiguities in this partitioning of space, which must be addressed. One must define both the radius for the metal sphere and the angles defining the cones of revolution in which the density is to be ascribed to a ligand. For neither parameter do we propose a rigorous, theoretically defined value. Rather, for the metal sphere we have taken the covalent radius of the metal, while for the ligands we have allowed them to be as large as possible with the restriction that they not overlap one another. While admittedly capricious, these assumptions are not so bad as one might initially suppose. Though covalent radii are empirical parameters, there is little difference between the radii of the second- and third-row transition metals.¹³ Since the intent of the method is to allow reliable interpretive comparisons, so long as one employs a consistent metal size, qualitative conclusions should not be markedly affected. Regarding definition of the ligand cone size, similar arguments are appropriate. The results should not vary drastically among reasonable choices in any case since

one would expect the centroid of charge to lie along the axis of the metal–ligand bond.

We now turn to a more detailed discussion of the exact nature of the modifications made to the Mulliken analysis. The total integrated density in a given orbital i may be written as

$$1 = \sum_{\mu \in M} \sum_{\nu \in M} C_{\mu i} C_{\nu i} S_{\mu\nu} + \sum_{\mu \in M} \sum_{\nu \in L} C_{\mu i} C_{\nu i} S_{\mu\nu} + \sum_{\mu \in L} \sum_{\nu \in L} C_{\mu i} C_{\nu i} S_{\mu\nu} \quad (2)$$

The first term constitutes density arising solely from metal-centered basis functions. The middle term involves one basis function from the metal and another from one of the ligands. The last term involves density arising entirely from ligand functions and is treated here in exactly the same manner as a conventional Mulliken analysis. The metal orbitals are however partitioned differently. The appropriation is based on a one-dimensional numerical quadrature for each basis function. This integration determines the percentage of a diagonal density term (e.g., $C_{\mu i}^2$), which is inside the metal radius; the remainder is divided among the ligands, the relative magnitudes determined by analytic, angular integrations. Off-diagonal metal terms are appropriated on the basis of a square-root interpolation preserving the functional form of the diagonal terms. The density terms involving one metal and one ligand basis function are treated similarly. As in a Mulliken analysis, half the density is said to belong to the ligand and is so appropriated. The other half, nominally the metal's density, is divided between the metal and ligands on the basis of the same criterion as the terms arising solely from metal orbitals.

These ideas are cast in terms of equations below. In analogy to eq 1, the total population of the metal atom is given by eq 3, where F_μ is a parameter specifying what percentage of the

$$Q_M = \sum_i^{\text{occ}} f_i \sum_{\mu \in M} \sum_{\nu} (F_\mu F_\nu)^{1/2} C_{\mu i} C_{\nu i} S_{\mu\nu} \quad (3)$$

density is to be assigned to the metal. For ligand-centered basis functions, $F_\nu = 1$; for metal-centered functions it is given by (the first term is the density inside the metal's covalent radius; the second term is the interstitial density):

$$F_\mu = I_\mu + (1 - G_\mu)(1 - I_\mu) \quad (4)$$

I_μ is the radial integral:

$$I_\mu = \int_0^{R_c} (\chi_\mu^2(r)) r^2 dr \quad (5)$$

χ_μ is the normalized radial component of basis function μ while R_c is the covalent radius of the metal. The parameter G_μ defines what fraction of the diagonal density arises from function μ at distances greater than R_c , which is in one of the ligand sections:

$$G_\mu = \sum_L G_{\mu L} \quad (6)$$

$$G_{\mu L} = \int_{\phi_{L1}}^{\phi_{L2}} d\phi \int_{\theta_{L1}}^{\theta_{L2}} (\sin \theta d\theta) (Y_\mu^*(\theta, \phi)) (Y_\mu(\theta, \phi)) \quad (7)$$

where the integration limits ϕ_L and θ_L define the cone of revolution for ligand L ; $Y_\mu(\theta, \phi)$ is the angular component of basis function μ .

The radial integrals of eq 5 were numerically evaluated (a contracted Gaussian basis set was used) with employment of Simpson's rule with 1000 intervals. When this technique is applied to the normalization integral ($R_c = \infty$), the resulting errors were less than 1 part per thousand. The angular integrals of eq 7 are easily evaluated analytically.

Once again, in analogy to eq 1, the expression for the charge assigned to a ligand, L, is given by eq 8, where $P_{\nu L}$ is the factor

$$Q_L = \sum_i^{\text{occ}} \left\{ \sum_{\mu \in L} \left[\sum_{\nu} C_{\mu i} C_{\nu i} S_{\mu\nu} + \sum_{\nu \in M} P_{\nu L} (1 - F_{\nu}^{1/2}) C_{\mu i} C_{\nu i} S_{\mu\nu} \right] + \sum_{\mu \in M} \sum_{\nu \in M} P_{\nu L} (1 - F_{\mu} F_{\nu})^{1/2} C_{\mu i} C_{\nu i} S_{\mu\nu} \right\} \quad (8)$$

that partitions the ligand density arising from metal basis functions among the various sections (see eq 9). The first

$$P_{\nu L} = G_{\mu L} / G_{\mu} \quad (9)$$

term in eq 8 is the normal Mulliken component to the population (i.e., eq 1). The second and third terms represent density that normally would have been assigned to the metal. The second term involves cross terms involving basis functions on both the metal and the ligand while the last term represents density arising solely from the metal basis functions. Consequently, these latter terms cannot be assigned to any basis function in particular but rather to only a ligand as a whole. As a result, terms requiring specific basis function assignment of charge density, for example, bond overlap populations, are not well-defined. This limitation is simply a manifestation of the fact that if basis functions centered on one atom yield densities, which in significant part are best appropriated to another atom (or ligand), constructs such as bond overlap may not prove to be particularly useful.

At this point, several comments regarding details implicitly but not necessarily apparently contained in the above equations seem necessary. First, for the maintenance of rotational invariance in the method, the orbital coefficient and overlap matrices must be expressed in a basis in which functions centered on the metal having different l quantum numbers are orthogonal. As an example simple Cartesian d functions cannot be used due to the nonzero overlap between the x^2 , y^2 , and z^2 functions with the s orbitals. Because of this overlap, individual ligands would receive populations from, for example, an $(x^2 - y^2, s)$ cross term even though the sum over all ligands would, of course be zero. As a result an $x^2 - y^2$ orbital in one orientation would not be equivalent to an xy orbital in an orientation rotated by 45° about the z axis. This problem is a trivial restriction: it does not require that the SCF be performed in an appropriate basis, only that a transformation to such a basis be performed prior to the population analysis.

A more serious consideration regarding the analysis is that the charge assigned to a particular ligand is not independent of the number of sections that are defined. As an example consider a linear ML_2 system. The most apparent choice would be to define two sections for the ligands. On the other hand, e.g., for comparison to a ML_4 system, one might wish to still define four sections, realizing that the density assigned to the extra two sections really belonged to the metal. The present analysis would not appropriate the same number of electrons to the ligands (or the metal) in the two cases even when the same orbitals are used. This inconsistency arises from the second term in eq 8. As an example, consider the component involving an s basis function on the metal (μ) and a ligand function (ν). With two sections (45° angles of revolution), the charge assigned to the ligand would be

$$\frac{1}{2}(1 - (1 - 2A - 2AI_{\mu})^{1/2})C_{\mu i}C_{\nu i}S_{\mu\nu}$$

with $A = 0.146447$. This expression may be verified by working through eq 8 and 9. If four sections were defined, the charge assigned to the ligand would be

$$\frac{1}{4}(1 - (1 - 4A + 4AI_{\mu})^{1/2})C_{\mu i}C_{\nu i}S_{\mu\nu}$$

These two expressions are obviously not identical. However, this inconsistency is empirically found to be rather small; the total charge assigned to a ligand typically differs by only a

Table I. Detailed Analyses for *trans*-Pt(PH₃)₂H₂

	modified Mulliken			modified Mulliken	
Pt	8.9868	10.4556	H ^a	1.4978	1.0826
s	0.4482	0.6096	s	1.0826	1.0826
x	0.3590	0.6815	from Pt	0.4152	
y	0.0949	0.1386	P	5.0440	4.7248
z	0.0157	0.0180	s	1.5387	1.5387
xy	1.6863	1.9578	x	0.8732	0.8732
xz	1.8544	1.9979	y	1.4353	1.4353
yz	1.8075	1.9534	z	0.8776	0.8776
$x^2 - y^2$	0.9418	3.0989	from Pt	0.3192	
$2z^2 - x^2 - y^2$	1.7862		H ^b	0.9866	0.9866
H ^a	1.4950	1.0798	H ^c	0.9898	0.9898
s	1.0798	1.0798			
from Pt	0.4152				

^a These hydrogens are the hydride ligands: they are different due to asymmetry introduced by phosphine hydrogens. ^b Phosphine hydrogen; in the metal-ligand plane. ^c Phosphine hydrogens; outside the metal-ligand plane.

few hundredths of an electron.

III. Exemplary Calculations

For the most part, discussion of the results obtained with use of the modified analysis will be deferred to the following paper, in which the chemistry of several square-planar systems will be discussed. Here we will present only rather cursory data chosen to demonstrate where differences arise between the present analysis and a conventional Mulliken analysis.

In Table I, a detailed comparison is made between analysis for an *ab initio* wave function describing *trans*-Pt(PH₃)₂H₂ (the reader is referred to the following paper regarding the basis set, effective core potential, and other details of the calculation). The covalent radius employed¹⁴ was 1.30 Å, and 45° angles of revolution were used to generate the ligand cones. The primary interest here is in determining which of the metal electrons are now being appropriated to ligands. As would be expected from the radial extent of the orbitals in Figure 1, an appreciable fraction of the density nominally arising from Pt s and p basis functions is so assigned within the modified analysis. Only 63% of the 1.45 e in such orbitals is assigned to the platinum atom. That it keeps even this percentage is surprising in view of the radial extent of the orbitals in Figure 1 and is evidence that the valence s and p orbitals are somewhat more contracted in the molecule than in the atom. It is important that there are a significant number of electrons occupying the s and p orbitals in what is nominally a d^8 state of the metal. This number is not atypical among the complexes that we have studied and is indicative that inclusion of diffuse functions in the basis set is necessary. As is also evident from Figure 1, the d density also extends beyond the covalent radius of the metal with a significant fraction more properly being appropriated to the ligands. In this present case, only 8.01 e of the 9.01 d electrons implied by a conventional Mulliken analysis are assigned to the platinum atom. As expected, the xy orbital (the ligands are situated along the x and y axes) donates the most significant portion of its charge to the ligands within this partitioning. Although it is tempting to ascribe this to metal-ligand π back-bonding, this does not principally represent a dynamic charge-transfer effect. Rather, it is a measure of the extent of the metal d orbitals.

Until now we have cited only the differences between our proposed modified analysis and a Mulliken assignment without actually considering whether we are indeed obtaining a better interpretation of the molecular wave function. Although we will defer most of our comments to the accompanying reports,

(14) F. R. Hartley, "The Chemistry of Palladium and Platinum", Wiley, New York, 1979, p 8.

several points can be made here. First the results of 1.02+ charge on the metal and 0.50- on the hydrogens are more in accord with the qualitative notion of the molecule as an oxidized metal atom with hydride ligands. Obviously one would not expect to see quite the demarcation of charge given by the formal description of +2 metal ion and 1- ligands. However, when compared with the description as virtually neutral hydrogens and a negatively charged metal in the standard analysis, the above picture appears more consistent with the chemical properties of the complex.

As a further check of the preceding analysis, a three-dimensional quadrature of the charge was performed within the sphere defining the metal region.¹⁵ For *trans*-Pt(PH₃)₂H₂ the value is obtained as 8.96 e compared with the 8.98 e given by the modified population analysis and 10.46 e by the Mulliken analysis. (The excellent quantitative agreement we have is partly fortuitous since in the population analysis we are also appropriating density to the metal that is outside its sphere but not within one of the ligand cones.) This additional evidence still provides a clear indication that the modified analysis is giving a more faithful representation of the wave

function than a standard analysis.

IV. Conclusions

The proposed modifications to a Mulliken analysis were found to resolve satisfactorily the interpretative difficulties resultant from the use of diffuse valence s and p basis functions, which are required to give reasonable theoretical descriptions of transition-metal systems. The method has two parameters that must be defined externally, the covalent radius of the metal atom and the solid angles defining the ligand space, and is currently limited to complexes having a single metal center. It requires very little additional computational effort to carry out such an analysis compared with that of traditional Mulliken population analysis. The results obtained thus far indicate the method yields an improved description of molecular charge densities, which should prove useful both in analyzing the results of theoretical calculations and in correlating with experimental probes of electron density in molecules.

Acknowledgment. The aid of S. Woodruff in implementing the three-dimensional quadrature is thankfully acknowledged. Thanks are also due to J. Hay for many helpful comments as well as a critical reading of the manuscript. This work was performed under the auspices of the U.S. Department of Energy.

Registry No. *trans*-Pt(PH₃)₂H₂, 76830-84-7.

(15) The integration scheme is outlined in: S. B. Woodruff and M. Wolfsberg, *J. Chem. Phys.*, **65**, 3687 (1976); *Chem. Phys. Lett.*, **56**, 125 (1978); H. Conroy, *J. Chem. Phys.*, **47**, 5307 (1967).

Contribution from the Theoretical Division, Los Alamos National Laboratory, University of California, Los Alamos, New Mexico 87545

Ab Initio Treatment of the Structures of Square-Planar Pt(PH₃)₂XY Species (X, Y = H, Cl) Using Relativistic Effective Core Potentials

J. OAKLEY NOELL* and P. JEFFREY HAY*

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The structures and relative energies of Pt(PH₃)XY isomers are investigated with use of ab initio molecular orbital theory and effective potentials. In particular, the *cis* and *trans* isomers of the dihydride, dichloride, and hydrochloride are studied. In all cases, the *trans* isomer is the more stable. Available experimental information is in good agreement with calculated bond lengths, bond angles, and vibrational frequencies.

I. Introduction

The intent of this work is to demonstrate that ab initio molecular orbital theory can provide useful geometric and energetic information for complexes involving third-row transition metals. The systems considered are the Pt(II) square-planar adducts Pt(PH₃)₂XY (where X, Y = H, Cl) and the product of their reductive elimination Pt(PH₃)₂. Since a subset of these have been well characterized both structurally and spectroscopically, these data may be used to evaluate the success of the technique (if we assume that we are afforded the liberty of replacing the substituted phosphine PR₃ by its parent hydride).

The question of the structures of platinum-hydride complexes deserves special consideration. The hydrogen is often not easily located through X-ray diffractometry, and as a result there is comparatively less data on platinum-hydrogen bond lengths. In addition, since very few *cis*-dihydride complexes of any kind have been observed experimentally, any suggestions calculations can offer regarding their structure and bonding should aid in their experimental characterization.

Finally these studies are to lay the ground work for an investigation of a prototype oxidative addition. Indeed the results of the present paper suggested the possibility of examining the H₂ + Pt(PH₃)₂ → *cis*-Pt(PH₃)₂H₂ reaction. It is in the arena of potential surfaces that ab initio calculations should have their greatest impact. This topic will be addressed in a later paper.¹

II. Method of Calculation

The calculations reported here were of the ab initio restricted Hartree-Fock (RHF) form. The [Xe]4f¹⁴ core of the platinum atom was, in all cases, replaced by a relativistic potential² derived according to the scheme of Kahn, Hay, and Cowan.³ The mass velocity and Darwin relativistic effects are included implicitly with the potential. As has been documented previously, these are critical in order to obtain the proper size and energy of the valence orbitals for metal atoms of the third transition series.⁴ The [Ne] cores of the phosphorus and

(1) J. O. Noell and P. J. Hay, in preparation.

(2) L. R. Kahn, Private communication.

(3) L. R. Kahn, P. Jeffrey Hay, and R. D. Cowan, *J. Chem. Phys.*, **68**, 2386 (1978).

(4) P. J. Hay, W. R. Wadt, L. R. Kahn, and F. W. Bobrowicz, *J. Chem. Phys.*, **69**, 984 (1978).

*Correspondence should be addressed either to J.O.N. at Division 8343, Sandia National Laboratory, Livermore, CA 94550, or to P.J.H. at Los Alamos National Laboratory.