Transferability of Atomic Hartree–Fock Valence-Shell Orbitals and Chemical Periodicity[1]

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Abstract: The atomic valence-shell Hartree–Fock orbitals of atoms in the same column of the periodic table are shown to be of at least the same size and, in a number of cases, to be nearly identical. This is done by comparing graphs of the Hartree–Fock orbitals and by calculating various energy integrals with them. The calculations have been carried out for all elements in the first four periods of the periodic table except the transition elements and for their singly charged negative ions. Before the comparisons are made, the valence orbitals of an atom are orthogonalized to the core orbitals of the atom lying below it in the periodic table, with whose valence orbitals the comparison is to be made. This causes the valence orbitals of the first atom to take on the same nodal structure as those of the second. It is shown that the valence orbitals of two atoms when compared in this way will be nearly identical if their ionization potentials are nearly equal, or if their Hartree–Fock valence-orbital energies are nearly equal.

It is shown in this paper that the valence-shell Hartree–Fock orbitals of atoms lying in the same column of the periodic table can be remarkably similar. The orbitals appear to reflect the chemical periodicity expressed by the periodic table. The similarities can be seen directly by comparing the orbitals graphically, and indirectly by comparing integrals calculated with the orbitals. This has been done for nearly all of the elements in the first four periods of the periodic table and their singly charged negative ions. The transition elements are the only ones omitted. That the Hartree–Fock valence-shell orbitals should exhibit such a chemical periodicity is believed to be of fundamental importance.

The importance of this property of Hartree–Fock orbitals lies in its practical, conceptual, and philosophical implications. The practical implication is that the calculation of molecular wave functions might be simplified considerably. This implication has already been discussed[2] in some detail in a more general context. The connection between that discussion and this paper will be made in a later section. The conceptual implication is that the interpretation and discussion of molecular wave functions in terms of atomic-like or localized orbitals and the periodic table, may be numerically justifiable in terms of the properties of Hartree–Fock orbitals. Furthermore the similarity of atomic valence shells implies that chemical systematics, the essence of chemistry, may mean more in quantum mechanics than that the valence shells of congeners have the same number of electrons. The philosophical implication is that chemical systematics may be found within quantum mechanics and that it need not be imposed on quantum mechanics as it has been in many semiempirical theories. The calculations reported in this paper are a first step toward understanding how chemical systematics is determined by quantum mechanics.

A more pragmatic justification for the study reported here lies in the complexity of the Hartree–Fock theory. The Hartree–Fock orbitals are self-consistent solutions to a set of nonlinear integrodifferential equations; they are not determined by fitting parameters to experiment. There is still much to be learned about such equations and the self-consistency process. Now that accurate Hartree–Fock orbitals are available for the elements in the first four periods of the periodic table,[3] we can learn empirically a little more about Hartree–Fock theory by experimenting with these orbitals, and in turn learn more about finding chemistry in quantum mechanics.

In this study the valence-shell orbitals are compared with a minimum of theoretical and mathematical manipulation. The goal of this paper is to establish the similarities of atomic valence-shell orbitals and understand why they are similar. The comparison is always of orbitals of congeners, *i.e.*, of atoms in the same column of the periodic table. The valence-shell Hartree–Fock orbitals of each atom are compared with the orbitals of all congeners lying below them in the first four periods. Before each comparison is made, the valence orbitals of the first atom are Schmidt-orthogonalized to the core orbitals of the congener, then normalized. This is done simply because the valence-shell orbitals of the second atom are orthogonal to its core orbitals and normalized. This process of Schmidt orthogonalization, normalization, and substitution is called *transfer by core orthogonalization.* Orbitals that have been transferred in this manner are referred to as *transfer* orbitals. The orbitals are compared graphically, so that point-by-point one can see qualitatively how similar the orbitals are, and where they differ most. A quantitative comparison is made by replacing the valence-shell orbitals of an atom A by the transfer orbitals from a congener B lying above it in the periodic table, then calculating all of the integrals needed to determine the total energy of atom A. The transferred orbitals are also compared to the valence orbitals of the atom to which the transfer is made by calculating the overlap integral of the orbitals. The overlap will be less than one unless the orbitals are identical. This is a convenient but rough test of the transferability of the valence-shell or-

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[2] W. H. Adams, *J. Chem. Phys.*, 42, 4030 (1965).

[3] (a) E. Clementi, *IBM J. Res. Develop.*, 9, 2 (1965); (b) P. S. Bagus and T. L. Gilbert have duplicated or improved slightly on Clementi's functions (private communication).

bitals. These several simple, direct methods of comparing the valence-shell Hartree–Fock atomic orbitals are used to establish the basic similarity of the orbitals of congeners and the remarkable similarities of third- and fourth-period congeners.

In the next section the programs that were used are described and their accuracy indicated. The following section summarizes the results of calculations using Clementi's neutral-atom Hartree–Fock orbitals.[3a] Then the same thing is done for the singly charged negative atomic ions. The relation of the orbital periodicities is discussed and explained in the next section. This section also contains a discussion of how the results of this study are related to the work of others, of how the present study can be refined, of the results of one such refined calculation, and of the relationship between atomic valence-orbital transferability and the transferability of localized orbitals from molecule to molecule.

Computer Programs

A set of FORTRAN computer programs has been written to carry out the various comparisons of valence-shell atomic orbitals. One program adjusts the coefficients given by Clementi[3a] so that the orbitals will be orthonormal to seven significant figures. The second program transfers the valence-shell orbitals from one atom to another by core orthogonalization, then makes graphs of the valence orbitals and the transferred orbitals. The third program also transfers valence-shell orbitals, then calculates the total energy of the atoms with the transferred and with the true valence-shell orbitals. The output from this program includes all of the integrals needed in the calculation of the total energy. This last program is of course the most elaborate of the three.

The first program was needed because Clementi's tables give the atomic eigenvectors to only five significant figures. Using the tabulated eigenvectors, it is not possible to reproduce Clementi's total energies for the fourth-period elements to five significant figures. Other integrals show a corresponding loss of accuracy. A simple expedient to regain the lost accuracy is to normalize the lowest energy eigenvector of each symmetry to the accuracy allowed by the computer, then to Schmidt-orthogonalize the next lowest energy eigenvector to the first and normalize that vector, and so on through the valence level.[4] The reorthonormalized vectors were specified to eight decimal places for these calculations, since the principal machine used was an IBM 7040. With these vectors Clementi's total energies could be reproduced to seven significant figures. This program was also used to check that the data cards were correctly punched. This was accomplished by requiring that the starting vectors be normalized to a degree consistent with the five-decimal accuracy of the tabulated orbitals.[3a]

The second program is also a quite simple one. It transfers the valence orbitals of each symmetry from atom A to a congener B lying further down the periodic table, by orthogonalizing the A vectors to the B core vectors, then normalizing the resultant vectors. The radial functions of the valence shell are then tabulated as a function of the radial distance r from the nucleus. Then for each symmetry a graph is made of the A and B radial functions and of the transferred radial function as functions of r. The program was written for an IBM 1620 with an attached CALCOMP plotter.[5] The program has been checked by comparing the calculated table of radial functions for several atoms with published tables for these atoms,[6] and by hand calculations.

The third program was the most difficult to write and debug. It calculates the total energy of each atom in a column of the periodic table, does all possible transfers of valence-shell orbitals down the column, and calculates the energy of each atom with the transferred valence orbitals substituted for its own. The program can handle up to five atoms in a column. All the integrals needed in the evaluation of the total energy as well as various important sums of these integrals and the overlap between the transferred and the true valence-shell orbitals are printed out and are punched on cards. The integrals are evaluated analytically using the formulas for the various atomic integrals over Slater basis functions. The program allows for the orbitals of any atom to be specified as linear combinations of up to 12 s, 10 p, and 8 d Slater orbitals. The accuracy of the program has been checked by comparing the total energies and the orbital eigenvalues to those tabulated by Clementi,[3a] and by checking, for several atoms, each integral calculated with Watson's orbitals against the integrals he tabulated.[7] Disagreement between the calculated values and the tabulated ones was confined always to the last or, for the larger integrals, next-to-last significant figure tabulated. This accuracy is quite sufficient for the purpose here. It also justifies the procedure used to reorthonormalize the tabulated eigenvectors.

The only unusual feature of the third program involves the calculation and utilization of the two-electron integrals. In calculations involving transfers of s and p valence orbitals from the third to the fourth period, over 127,000 distinct two-electron integrals over the Slater basis sets have to be evaluated. The contribution of each distinct integral over the basis to the Slater F and G integral over the Hartree–Fock and transferred orbitals is evaluated before the next integral over the basis set is calculated. (This was a necessity in the earliest versions of the program, since they were written for the Pennsylvania State University's IBM 7074, which had only a 10K core. In the IBM 7040 version the integrals over the basis set are temporarily stored in core until there are 10,000 of them; then they are put on tape. The integrals are then available for use in a more sophisticated transferability calculation, which will be described elsewhere.) Since more than 127,000 integrals have to be combined, there is a good chance that roundoff and truncation errors can invalidate the calculations. On the IBM 7040 this happened. The difficulty was overcome by putting large contributions to the Slater integrals over the Hartree–Fock and transfer orbitals into one sum, the small contributions into a second sum, and, as the last step in the calculation, combining the two sums.[8]

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(4) This procedure was suggested by Dr. P. S. Bagus.

(5) These calculations were done at the Argonne National Laboratory.

(6) C. C. J. Roothaan, L. M. Sachs, and A. Weiss, *Rev. Mod. Phys.*, **32**, 186 (1960).

(7) R. E. Watson, Massachusetts Institute of Technology Solid State and Molecular Theory Group, Technical Report 12, June 15, 1959 (unpublished).

The formal mathematical analysis on which the third program was based was derived from various sources. The one-electron integrals are evaluated using the formulas given by Roothaan and Bagus.[9] The analytic formulas for the two-electron integrals over the basis set were developed by me, so that the program could calculate the Slater F and G integrals from them. The total energy is calculated from the one-electron and two-electron integrals according to the analysis given by Slater.[10] The orbital energies are evaluated as expectation values of the Hartree–Fock Hamiltonians, not by diagonalizing the closed- and open-shell Hamiltonians. It is gratifying to find that the orbital energies calculated in this way, using the reorthonormalized vectors, agree with the values given by Clementi.

Neutral Atoms

There is an infinite number of ways in which the Hartree–Fock valence-shell orbitals of congeners might be compared. The ways chosen to be used are ones which seem to make very direct comparisons, or which answer questions raised by the first comparisons. Before discussing the results of each of the numerical experiments described here, an indication is given of the reason that calculation was made. The discussion is meant to bring out the salient features of the tables and graphs.

In Table I the portion of the periodic table pertinent to this study is given in a form which deviates from the usual form in only one respect. The deviation occurs in the fourth period. K and Ca have been placed in a row by themselves, with Cu and Zn directly below them. This has been done because the elements Cu through Kr in their ground states have the same core configuration, *i.e.*, $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(3d)$.[8] The elements K and Ca of course have no occupied d orbitals. In addition Cu and Zn have the same outer-shell configuration as the other elements in the column to which they have been assigned. Thus in terms of electronic structure it makes sense to group the elements this way, although chemically we know that Cu and Zn are quite different from the elements with which they are grouped. This portion of the periodic table will be referred to in each of the following calculations. The calculations have been carried out for all those symmetry states derivable from the ground-state configuration for which Clementi has calculated Hartree–Fock orbitals.

Table I. Periodic Table of the Elements As Used in This Study

Period	I	II	III	IV	V	VI	VII	VII
1	H							He
2	Li	Be	B	C	N	O	F	Ne
3	Na	Mg	Al	Si	P	S	Cl	Ar
4a	K	Ca						
4b	Cu	Zn	Ga	Ge	As	Se	Br	Kr

The first comparison of the valence orbitals of congeners is relatively crude, although it has certain advantages. The valence-shell orbitals of each symmetry for an atom A_i in the *i*th row are transferred by core orthogonalization (see earlier text) to a congener A_j in the *j*th row of the periodic table ($j > i$); then the overlap of the transferred orbital $\psi_T(i\rightarrow j)$ and the true valence-shell orbital $\psi_V(j)$ are calculated. If $\psi_T(i\rightarrow j)$ and $\psi_V(j)$ are identical then the magnitude of the overlap will be one. If the orbitals differ, then as is well known, the overlap integral will be less than one in magnitude, *i.e.*

$$|\langle\psi_T(i\rightarrow j)|\psi_V(j)\rangle| < 1$$

One advantage of looking at this integral is that it has an optimum value which is independent of the atoms that are being compared, so that all pairs are compared on an equal basis. The second advantage is that the orbitals are compared primarily where they are largest, since those regions contribute most strongly to the integral.

In Table II the integrals $|\langle\psi_T(i\rightarrow j)|\psi_V(j)\rangle|$ for s orbitals are given; in Table III, those for p orbitals. H and He have been omitted from the tables. The former was omitted because its overlap with the valence orbitals of its congeners was in no case larger than 0.84, showing that it is quite different from its congeners. On the other hand the He 1s orbital can be quite similar to the valence s orbitals of its congeners, but it of course has no p valence orbital as does its congeners, so that their valence shells cannot be fully compared. (In the interest of completeness, the overlap integrals involving He are He → Ne, 0.98534; He → Ar, 0.99265; He → Kr, 0.98635.) The Roman numeral table headings refer to the colums of the periodic table given in Table I. The spectroscopic symbol in parentheses which follows the Roman numeral indicates the symmetry of the ground-state configuration recorded in that column. The row headings indicate the transfers that were made by giving the period labels from Table I.

The basic implications of the two tables are that second- and third-period congeners have valence orbitals of about the same size, and that period 3 and period 4b congeners are very similar in columns III through VI. The largest overlap integrals are found between ψ_T(Si→Ge) and ψ_V(Ge) for both s and p orbitals. The problem now is to determine what the various values of $\langle\psi_T|\psi_V\rangle$ imply.

A direct way to see what the overlap integral $\langle\psi_T|\psi_V\rangle$ means is to plot ψ_T and ψ_V so that they can be compared point by point. Since we are dealing with atoms, it is only necessary to plot the radial functions for each symmetry. In the usual fashion[3a] the orbitals are written as functions of spherical coordinates r, θ, ϕ with the origin at the atomic nucleus.

$$\psi_{nlm} = R_{nl}(r)\Theta_{lm}(\theta,\phi)$$

The function Θ_{lm} is the normalized spherical harmonic. The radial function $R_{nl}(r)$ is normalized, *i.e.*

$$\int_0^\infty |R_{nl}(r)|^2 r^2 dr = 1$$

The graphs have plots of

$$P_{nl}(r) = rR_{nl}(r)$$

as a function of r. The graphs presented are representative of those obtained. They indicate quite clearly what the overlap integrals in Tables II and III imply.

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(8) This technique has been described in an article by I. Shavitt in "Methods in Computational Physics," Vol. II, Academic Press, New York, N. Y., 1963, p 1.

(9) C. C. J. Roothaan and P. S. Bagus in "Methods in Computational Physics," Vol. II, Academic Press, New York, N. Y., 1963, p 47.

(10) J. C. Slater, "Quantum Theory of Atomic Structure. II," McGraw-Hill Book Co., Inc., New York, N. Y., 1960.

Table II. Overlap Integrals $\langle\psi_T(i\rightarrow j)|\psi_V(j)\rangle$ for s Orbitals of Neutral Atoms

	I	II	III	IV (^{3}P)	IV (^{1}D)	V (^{4}S)	V (^{2}D)
2-3	0.99500	0.97385	0.95734	0.94420	0.94349	0.93384	0.93305
2-4a	0.94980	0.91339					
3-4a	0.96675	0.95748					
2-4b	0.98499	0.99676	0.97797	0.95791	0.95727	0.94183	0.94107
3-4b	0.96376	0.98880	0.99783	0.99946	0.99946	0.99755	0.99751
4a-4b	0.81345	0.83313					

	V (^{2}P)	VI (^{3}P)	VI(^{1}D)	VI (^{1}S)	VII	VIII
2-3	0.93254	0.92487	0.92442	0.92382	0.91817	0.91313
2-4a						
3-4a						
2-4b	0.94055	0.92917	0.92879	0.92824	0.92086	0.91584
3-4b	0.99748	0.99384	0.99383	0.99379	0.98943	0.98473
4a-4b						

Table III. Overlap Integrals $\langle\psi_T(i\rightarrow j)|\psi_V(j)\rangle$ for p Orbitals of Neutral Atoms

	III	IV (^{3}P)	IV (^{1}D)	V (^{4}S)	V (^{2}D)	V (^{2}P)
2-3	0.92623	0.92620	0.93179	0.92603	0.93116	0.93447
2-4a						
3-4a						
2-4b	0.93386	0.92470	0.93046	0.91860	0.92446	0.92818
3-4b	0.99987	0.99899	0.99900	0.99603	0.99621	0.99631
4a-4b						

	VI (^{3}P)	VI (^{1}D)	VI (^{1}S)	VII	VIII
2-3	0.93209	0.93437	0.93762	0.93513	0.93718
2-4a					
3-4a					
2-4b	0.92290	0.92563	0.92958	0.92574	0.92865
3-4b	0.99254	0.99264	0.99289	0.98874	0.98501
4a-4b					

In Figure 1 the Li 2s and Na 3s radial functions P(r) are plotted against r. It is quite clear that there are important differences between these two functions for small r, but that for large r the two functions are nearly equal. (For this reason the other graphs are given on a larger scale, with the tails of the functions cut off.) The Li → Na transfer orbital differs from the Na 3s on the graph for large r to the same degree that the Li 2s did, but for small r it has nodes in approximately the same places as the Na 3s. Thus as one would have expected, transfer by core orthogonalization changes a radial function primarily at small r, *i.e.*, in the atomic core region. The magnitude of the maximum and the minimum of the Na 3s function in the core region are overestimated by the Li → Na transfer orbital. Nevertheless the transfer orbital and the Na 3s orbital are, in the opinion of the author, surprisingly similar.

The transfer which produced the largest overlap integrals in Tables II and III was from Si to Ge. In Figures 2 and 3 are displayed, respectively, the s and p orbitals for the atoms in the ^{3}P state. The Si 3s orbital is clearly more accurately transferable to Ge than is the Si 3p. Core orthogonalization has put nodes into the radial functions in very nearly the correct positions. In Figures 4 and 5 similar results are given for P and As. The overlap integrals of the P → As s and p transfer orbitals with the As 4s and 4p orbitals, respectively, are the second-largest given in Tables II and III. The accuracy of the transfer in this case appears in the graphs to be not so good as in the Si → Ge case.

The meaning of overlaps of the order of magnitude of 0.995 and larger should be clear now. When the overlap of transferred and true valence orbitals is of the order of magnitude of 0.96, the most that can be said is that the pairs of orbitals are roughly the same size.

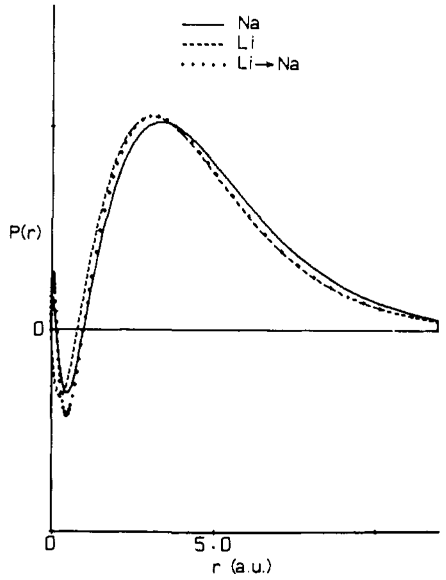

Figure 1. Radial parts of the Li 2s and Na 3s Hartree–Fock orbitals, and the Li → Na transfer orbital.

Overlaps this small are typical for second- to third-period transfers. In Figures 6 and 7 a comparison of the C, Si, and C → Si radial functions is made.

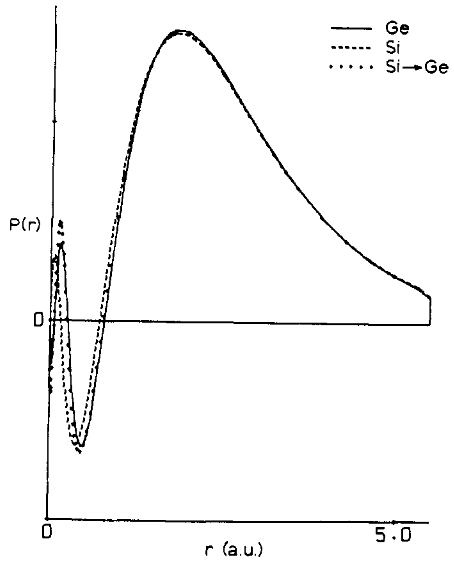

Figure 2. Radial parts of the Si 3s and Ge 4s Hartree-Fock orbitals for the ^3P state, and the Si → Ge s transfer orbital.

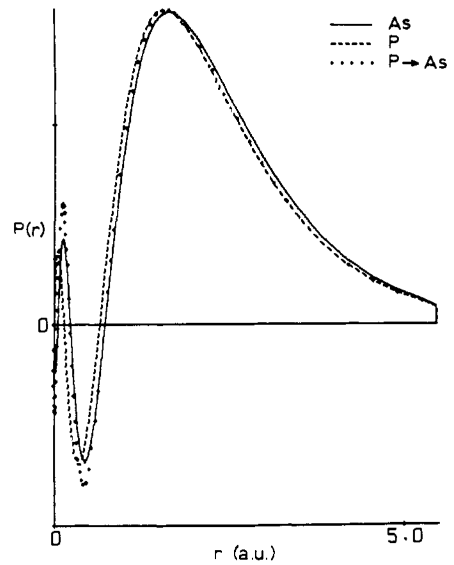

Figure 4. Radial parts of the P 3s and As 4s Hartree-Fock orbitals for the ^4S state, and the P → As s transfer orbital.

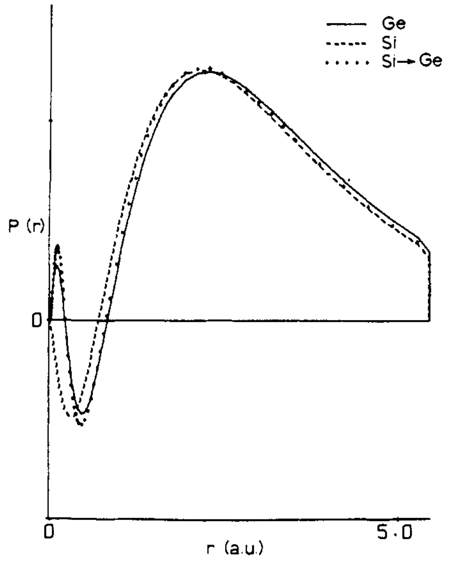

Figure 3. Radial parts of the Si 3p and Ge 4p Hartree-Fock orbitals for the ^3P state, and the Si → Ge transfer orbital.

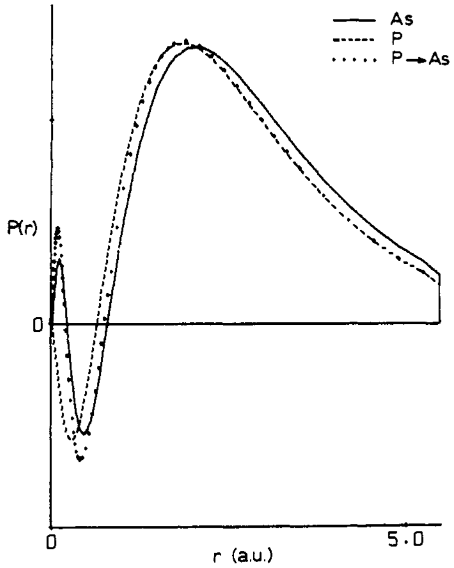

Figure 5. Radial parts of the P 3p and As 4p Hartree-Fock orbitals for the ^4S state, and the P → As p transfer orbital.

The conclusion that may be drawn from Tables II and III and the graphs is that for transfers from the third period to period 4b in columns III to VII, the transfer orbitals are qualitatively good approximations to the true valence orbitals of period 4b. This raises the question of how accurate an approximation they are when it comes to evaluating integrals.

The first quantitative comparison is between the valence-orbital eigenvalues and the expectation values of the Fock operators calculated with the transferred orbitals. (These should be good approximations to the eigenvalues one would get using as basis set the valence orbitals of one atom and the core orbitals of its congeners.) These energies are quite important since they appear in both the ionization potentials and the total energies. In addition, in these integrals errors in the kinetic energy are balanced against those in the nuclear potential energy and the coulomb and exchange integrals, thus giving an overall picture of the accuracy to which the transferred orbitals approximate the true orbitals. These integrals are quite sensitive to errors in the orbitals, but not so sensitive as the kinetic energy integrals. Energy calculations have been carried out only in those cases in which $|\langle\psi_T(i\rightarrow j)|\psi_V(j)\rangle| > 0.99$ for the valence-shell orbitals. (This cutoff value of the overlap was determined arbitrarily on the basis of experience, as the point beyond which the integrals would be quite inaccurate.) This condition was satisfied by transfers from period 3 to period 4b in columns III–VI of the periodic table. In column I, however, only the transfer from period 2 to period 3 had an overlap greater than 0.99. In column II of Table II the only transfer having an overlap greater than 0.99 was Be → Zn. The orbital energies in columns I and II in Table IV are for the Li → Na and Be → Zn transfers. The results of the orbital energy calculations are recorded in Tables IV and V.

Table IV. Neutral Atom Valence Orbital Energies (au) for s Symmetry

	I[a]	II[b]	III	IV (^{3}P)	IV (^{1}D)	V (^{4}S)
Row 3	−0.1963	−0.3093	−0.3935	−0.5399	−0.5476	−0.6964
Row 4b	−0.1821	−0.2925	−0.4245	−0.5533	−0.5609	−0.6859
3-4b	−0.1635	−0.2615	−0.3783	−0.4515	−0.4584	−0.4917

	V (^{2}D)	V (^{2}P)	VI (^{3}P)	VI (^{1}D)	VI (^{1}S)
Row 3	−0.7065	−0.7134	−0.8796	−0.8859	−0.8957
Row 4b	−0.6952	−0.7016	−0.8373	−0.8429	−0.8517
3-4b	−0.5000	−0.5056	−0.5102	−0.5151	−0.5226

[a] These data are for Li, Na, and Li → Na. [b] These data are for Be, Zn, and Be → Zn.

Table V. Neutral Atom Valence Obital Energies (au) for p Symmetry

	III	IV (^{3}P)	IV (^{1}D)	V (^{4}S)	V (^{2}D)
Row 3	−0.2102	−0.2971	−0.2609	−0.3917	−0.3506
Row 4b	−0.2085	−0.2873	−0.2518	−0.3695	−0.3302
3-4b	−0.2144	−0.2680	−0.2326	−0.2982	−0.2594

	V (^{2}P)	VI (^{3}P)	VI (^{1}D)	VI (^{1}S)
Row 3	−0.3243	−0.4374	−0.4154	−0.3835
Row 4b	−0.3050	−0.4028	−0.3822	−0.3524
3-4b	−0.2346	−0.2520	−0.2318	−0.2029

The general picture that emerges from Tables IV and V is that the orbital energies are quite sensitive to small errors in the orbitals. In every case the energy calculated with the transferred orbitals is smaller than the true energy. (It is interesting to note that the energies calculated with the nonorthogonalized orbitals are generally closer to the true values than those calculated with the orthogonalized orbitals. However, they must be orthogonalized to the cores.) The greatest accuracy for s orbitals is about 10%, for p orbitals about 3%. The largest errors are of the order of 50%. In general it does not appear that the transferred orbitals can be used in place of the true valence-shell orbitals to calculate the valence orbital energies of an atom accurately.

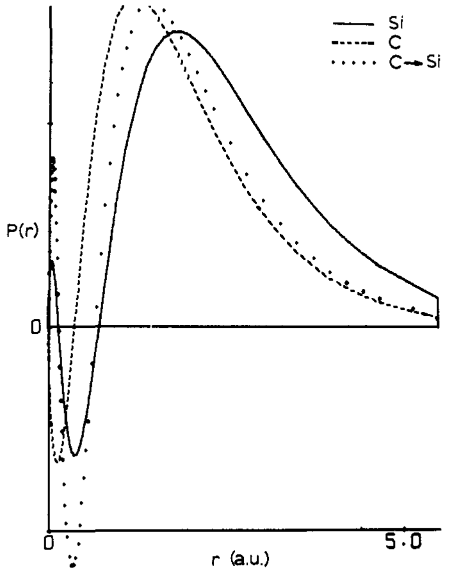

Figure 6. Radial parts of the C 2s and Si 3s Hartree–Fock orbitals for the ^{3}P state, and the C → Si s transfer orbital.

Similar conclusions can be drawn from the kinetic energy integrals presented in Tables VI and VII. These integrals are very inaccurate, being always too large by at least 40%. Clearly there are gross differences between the transferred and true valence-shell orbitals as far as the kinetic energy operator is concerned. However, we know from the graphs that when $\langle|\psi_T(i\rightarrow j)|\psi_V(j)\rangle| > 0.995$ the big differences between the transferred and true orbitals occur in the core region. This point will be taken up in a later section.

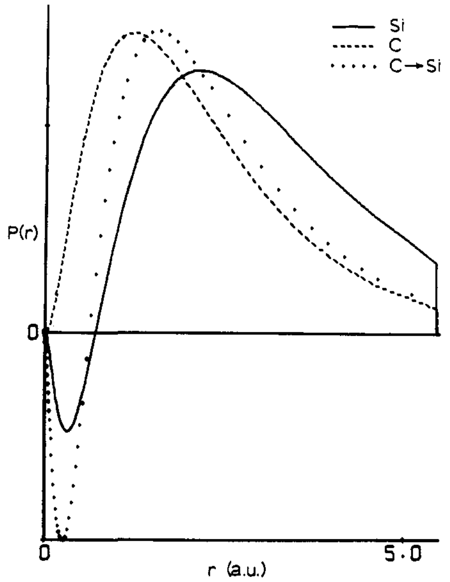

Figure 7. Radial parts of the C 2p and Si 3p Hartree–Fock orbitals for the ^{3}P state, and the C → Si p transfer orbital.

The next integrals to be compared are the Slater integrals $F^0(nl,nl)$ calculated with the transferred and true valence-shell orbitals. Let $r_>$ be the larger of the two variables r_1 and r_2; then

$$F^0(nl,nl) = \int_0^\infty dr_1 r_1^2 \int_0^\infty dr_2 r_2^2 [R_{nl}(r_1)]^2 [R_{nl}(r_2)]^2 \frac{1}{r_>}$$

Table VI. Neutral Atom Valence Orbital Kinetic Energies (au) for s Symmetry

	I[a]	II[b]	III	IV (^{3}P)	IV (^{1}D)	V (^{4}S)
Row 3	0.2088	0.5011	0.9352	1.3856	1.3956	1.8903
Row 4b	0.2673	1.0219	1.5000	1.9879	2.0011	2.4977
3-4b	0.5954	1.4693	2.0788	3.5494	3.5763	5.3489
	V (^{2}D)	V (^{2}P)	VI (^{3}P)	VI (^{1}D)	VI (^{1}S)	
Row 3	1.9035	1.9125	2.4717	2.4795	2.4922	
Row 4b	2.5128	2.5225	3.0558	3.0664	3.0799	
3-4b	5.3882	5.4153	7.5210	7.5462	7.5879	

[a] These data are for Li, Na, and Li → Na. [b] These data are for Be, Zn, and Be → Zn.

Table VII. Neutral Atom Valence Orbital Kinetic Energies (au) for p Symmetry

	III	IV (^{3}P)	IV (^{1}D)	V (^{4}S)	V (^{2}D)
Row 3	0.5714	0.9406	0.9107	1.3638	1.3363
Row 4b	0.7735	1.1908	1.1527	1.6309	1.5986
3-4b	0.8932	1.7343	1.6802	2.8114	2.7559
	V (^{2}P)	VI (^{3}P)	VI (^{1}D)	VI (^{1}S)	
Row 3	1.3182	1.8067	1.7963	1.7804	
Row 4b	1.5762	2.0618	2.0505	2.0341	
3-4b	2.7191	4.0216	3.9990	3.9645	

Table VIII. Slater Integrals F^0 over s Valence Orbitals of Neutral Atoms (au)

	I[a]	II[b]	III	IV (^{3}P)	IV (^{1}D)	V (^{4}S)
Row 3	0.23400	0.34323	0.34808	0.41004	0.41114	0.46797
Row 4b	0.21527	0.31318	0.36401	0.40659	0.40756	0.44549
3-4b	0.23271	0.33329	0.34658	0.40788	0.40897	0.46501
	V (^{2}D)	V (^{2}P)	VI (^{3}P)	VI (^{1}D)	VI (^{1}S)	
Row 3	0.46916	0.47000	0.52544	0.52604	0.52702	
Row 4b	0.44646	0.44713	0.48344	0.48392	0.48468	
3-4b	0.46619	0.46703	0.52152	0.52212	0.52310	

[a] These data are for Li, Na, and Li → Na. [b] These data are for Be, Zn, and Be → Zn.

Table IX. Slater Integrals F^0 over p Valence Orbitals of Neutral Atoms (au)

	III	IV (^{3}P)	IV (^{1}D)	V (^{4}S)	V (^{2}D)
Row 3	0.26459	0.32961	0.32173	0.39048	0.38342
Row 4b	0.26560	0.31650	0.30894	0.36078	0.35432
3-4b	0.26319	0.32673	0.31890	0.38559	0.37854
	V (^{2}P)	VI (^{3}P)	VI (^{1}D)	VI (^{1}S)	
Row 3	0.37863	0.44068	0.43740	0.43227	
Row 4b	0.34991	0.39439	0.39141	0.38688	
3-4b	0.37376	0.43322	0.42994	0.42481	

Like the kinetic energy integral, $F^0(nl,nl)$ depends only on a single orbital. Tables VIII and IX show the values which have been calculated. Clearly F^0 is much less sensitive to details of the orbitals than are the other integrals considered. The largest error made when the transferred orbitals are substituted for the true valence-shell orbitals is approximately 10%. The effect of core orthogonalization on F^0 is small; it changes F^0 by about 1%. It is, by the way, only in this case that orthogonalization to the core improves the value of the integrals.

The total electronic energies calculated with the true Hartree–Fock orbitals and the same energy calculated with the transferred orbitals substituted for the true orbitals are presented in Table X. Since the total energy is relatively insensitive to errors in the wave function, it cannot tell one much about the quality of the transferred orbitals; however, for completeness they obviously must be included. The smallest error is about 0.02, the largest about 0.7 au. Considering the magnitude of the errors in the orbital energies and that they enter the total energy multiplied by occupation numbers, the error in the total energy is reasonable. Note also that the energy found with the transferred orbitals is always higher than that found when the true valence-shell orbitals are used.[11] This is to be expected of course if Clementi's expansion Hartree–Fock orbitals are accurate.

The data displayed in this section are easily summarized. The basic conclusions are that in columns III through VIII of the periodic table, the valence-shell orbitals of second- and third-period elements are about the same size, and that in the same columns the valence-shell orbitals of the third and fourth periods (period 4b in Table I) are remarkably similar. The exceptions to these conclusions lie in columns I and II of the periodic table. The Li 2s and Na 3s orbitals are quite similar; the Be 2s and Zn 4s orbitals are also very close. As was indicated earlier H is really quite different from its congeners, but He is not. The 1s He orbital is at least about the same size as the valence s orbitals of the other rare gases. An attempt is made later in the text to understand these results and to correlate them with the experimentally known properties of the atoms.

Negative Atomic Ions

The same comparisons that were made of the valence-shell orbitals of the neutral atoms can be made of those of the singly charged negative atomic ions. The results of this comparison indicate that transferability depends little upon the total atomic charge and the tightness with which the electrons are bound. Clementi's negative-ion Hartree–Fock orbitals are used.[3a] Comparisons are made for nearly all of the symmetry states derivable from the ground-state configurations of the negative ions of atoms in the first four periods of the periodic table.

In Tables XI and XII the overlap integrals $\langle\psi_T(i\rightarrow j)|\psi_V(j)\rangle$ are given for s and p valence orbitals, re-

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(11) In a preliminary report on this work presented at the Edmonton. Quantum Chemistry Symposium in Aug 1965, some total energies were reported which were significantly lower than Clementi's Hartree–Fock energies. At the time it was not clear that my numbers were incorrect. Later an error was found in my computer program.

Table X. Total Electronic Energies (au) for Neutral Atoms

	I[a]	II[b]	III	IV (^{3}P)	IV (^{1}D)	V (^{4}S)
Period 4b	−161.859	−1777.847	−1923.260	−2075.359	−2075.321	−2234.238
3-4b	−161.840	−1777.805	−1923.142	−2075.166	−2075.116	−2233.854

	V (^{2}D)	V (^{2}P)	VI (^{3}P)	VI (^{1}D)	VI (^{1}S)
Period 4b	−2234.171	−2234.128	−2399.867	−2399.818	−2399.746
3-4b	−2233.787	−2233.744	−2399.165	−2399.117	−2399.045

[a] In I the data are for Na and Li → Na. [b] In II the data are for Zn and Be → Zn.

Table XI. Overlap Integrals $\langle\psi_T(i\rightarrow j)|\psi_V(j)\rangle$ for s Orbitals of Negative Atomic Ions

	I	III (^{3}P)	III (^{1}D)	IV (^{4}S)	IV (^{2}D)	IV (^{2}P)
2-3	0.99691	0.96572	0.96381	0.95288	0.95090	0.95045
2-4a	0.97422					
3-4a	0.97906					
2-4b	0.98017	0.98434	0.98284	0.96633	0.96452	0.96398
3-4b	0.96649	0.99747	0.99763	0.99948	0.99947	0.99948
4a-4b	0.86472					

	V (^{3}P)	V (^{1}D)	V (^{1}S)	VI	VII
2-3	0.94067	0.93993	0.93854	0.93019	0.92492
2-4a					
3-4a					
2-4b	0.94954	0.94873	0.94742	0.93550	0.92955
3-4b	0.99781	0.99775	0.99774	0.99443	0.99024
4a-4b					

Table XII. Overlap Integrals $\langle\psi_T(i\rightarrow j)|\psi_V(j)\rangle$ for p Orbitals of Negative Atomic Ions

	III (^{2}P)	III (^{1}D)	IV (^{4}S)	IV (^{2}D)	IV (^{2}P)
2-3	0.96148	0.96916	0.95426	0.96024	0.96360
2-4a					
3-4a					
2-4b	0.96314	0.97162	0.95433	0.96070	0.96434
3-4b	0.99970	0.99979	0.99931	0.99935	0.99938
4a-4b					

	V (^{3}P)	V (^{1}D)	V(^{1}S)	VI	VII
2-3	0.95678	0.95912	0.96291	0.95698	0.95646
2-4a					
3-4a					
2-4b	0.95475	0.95761	0.96214	0.95427	0.95401
3-4b	0.99727	0.99735	0.99749	0.99432	0.99110
4a-4b					

spectively. The regularities found for the neutral atoms persist. The overlap integrals have nearly all increased, but for the most part by less than 1%.

So that a comparison can be made with the neutral atoms, Figure 8 displays the functions $P_{nl}(r)$ for the Li^- and Na^- valence shells and the transfer orbital. Clearly the effect of adding an electron has been to make the orbitals spread out without greatly altering their close resemblance.

Data to match those for the neutral atoms are presented in Tables XIII-XIX. Inspection of these results show that the extra electron has had but a small effect on the transferability of the valence-shell orbitals. The regularities found match those found for netural atoms. There is accordingly no need to comment on these tables.

Discussion

The results displayed earlier clearly show that the valence-shell orbitals of second- and third-period elements are at least of about the same size, and that the valence-shell orbitals of third- and fourth-period elements can be remarkably similar. In this section these results are discussed, interpreted, and related to a physical property of the atoms. In addition the relationship of this study to other studies is indicated, and some further studies are proposed.

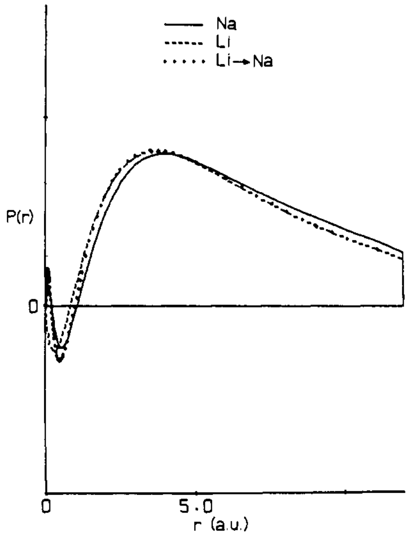

Figure 8. Radial parts of the Li^- 2s and Na^- 3s Hartree–Fock orbitals, and the $Li^- \rightarrow Na^-$ transfer orbitals.

The observed regularities occasionally contradict what one might have expected to be observed. In the case of the alkali metals, for example, quite different results were expected. It was anticipated that if the Li 2s and the Na 3s orbitals were as similar as they turned out to be, the Na 3s and K 4s orbitals would be still more similar. In all three, at large distances from the

Table XIII. Negative Atomic Ion Valence Orbital Energies (au) for s Symmetry

	I[a]	III (^{3}P)	III (^{1}D)	IV (^{4}S)	IV (^{2}D)	IV (^{2}P)
Row 3	−0.0145	−0.2080	−0.2308	−0.3015	−0.3200	−0.3338
Row 4b	−0.0126	−0.2390	−0.2615	−0.3194	−0.3377	−0.3517
3–4b	0.0007	−0.1952	−0.2173	−0.2231	−0.2398	−0.2524
	V (^{3}P)	V (^{1}D)	V (^{1}S)	VI	VII	
Row 3	−0.4364	−0.4473	−0.4623	−0.5794	−0.7329	
Row 4b	−0.4384	−0.4483	−0.4621	−0.5598	−0.6855	
3–4b	−0.2479	−0.2572	−0.2698	−0.2369	−0.1926	

[a] These data are for Li^-, Na^-, and $Li^- \rightarrow Na^-$.

Table XIV. Negative Atomic Ion Valence Orbital Energies (au) for p Symmetry

	III (^{3}P)	III (^{1}D)	IV (^{4}S)	IV (^{2}D)	IV (^{2}P)
Row 3	−0.0198	−0.0053	−0.0616	−0.0385	−0.0252
Row 4b	−0.0178	−0.0034	−0.0590	−0.0363	−0.0237
3–4b	−0.0236	−0.0087	−0.0425	−0.0200	−0.0072
	V (^{3}P)	V (^{1}D)	V (^{1}S)	VI	VII
Row 3	−0.0769	−0.0643	−0.0455	−0.1074	−0.1499
Row 4b	−0.0733	−0.0609	−0.0424	−0.1013	−0.1389
3–4b	−0.0084	0.0032	0.0206	0.0393	0.1039

Table XV. Negative Atomic Ion Valence Orbital Kinetic Energies (au) for s Symmetry

	I[a]	III (^{3}P)	III (^{1}D)	IV (^{4}S)	IV (^{2}D)	IV (^{2}P)
Row 3	0.1011	0.8549	0.8804	1.2675	1.2906	1.3070
Row 4b	0.1306	1.3939	1.4276	1.8337	1.8642	1.8874
3–4b	0.2878	1.8991	1.9574	3.2434	3.3043	3.3476
	V (^{3}P)	V (^{1}D)	V (^{1}S)	VI	VII	
Row 3	1.7736	1.7869	1.8061	2.3304	2.9431	
Row 4b	2.3541	2.3679	2.3924	2.8905	3.4557	
3–4b	5.0178	5.0563	5.1127	7.0884	9.4410	

[a] These data are for Li^-, Na^-, and $Li^- \rightarrow Na^-$.

Table XVI. Negative Atomic Ion Valence Orbital Kinetic Energies (au) for p Symmetry

	III (^{3}P)	III (^{1}D)	IV (^{4}S)	IV (^{2}D)	IV (^{2}P)
Row 3	0.3631	0.3263	0.7151	0.6839	0.6626
Row 4b	0.4789	0.4311	0.9040	0.8641	0.8370
3–4b	0.5549	0.4992	1.2991	1.2442	1.2062
	V (^{3}P)	V (^{1}D)	V (^{1}S)	VI	VII
Row 3	1.0783	1.0647	1.0460	1.5121	1.9910
Row 4b	1.2911	1.2750	1.2529	1.7283	2.1887
3–4b	2.1988	2.1720	2.1351	3.3344	4.6381

nucleus an electron sees a unit, net positive charge on the atom. In addition, in going down a column of the periodic table, the number of core orbitals increases, so that the properties of the valence orbital in the core region should be increasingly determined by the core orbitals.[12] (Differences in the valence orbitals due to the core orbitals are rather naively taken care of by the transfer-by-core-orthogonalization procedure.) The overlap integrals given in Table II contradicted expectation (graphs of the alkali orbitals emphatically contradicted expectation); the reason for this was not understood. It was speculated that the absence of d core orbitals in K might explain the result. Perhaps what was required was that each possible inner shell be completely filled. The results in Table II for the transfers Li to Cu and Na to Cu are sufficient to do away with that speculation.

In column II the transferability relations again are contradictory, but in columns III–VIII there is great regularity. However, in spite of the great similarity between the Si and Ge valence shells, the energy integrals calculated with the transferred orbitals for the most part are disappointing in their accuracy. In view of the pragmatic approach to transferability which has been adopted in this paper, this should not be altogether surprising. The transfer-by-core-orthogonalization procedure does succeed usually in making the behavior, for example, of the Si valence orbitals in the core region of Ge more similar to that of the Ge valence orbitals. Unfortunately this pragmatic approach does not remove the dependence on the Si core orbitals from the valence orbitals which are transferred from Si. There are ways of doing this.[13]

A direct way of removing from a transferred orbital its dependence on the core orbitals of the atom from which it is taken, and orthogonalizing it to the core orbitals of the atom to which it is transferred, has been investigated. The transferred orbital $\psi_T(i \rightarrow j)$ is chosen to be that linear combination of the core and valence orbitals of atom i, and of the core orbitals of j, which maximizes its overlap with the valence orbital $\psi_V(i)$ of j. This is accomplished mathematically by projecting $\psi_V(j)$ on the space spanned by the occupied orbitals of i and the core orbitals of j.[14] The resultant improvements of this projective transfer method over the core orthogonalization method are small for the overlap integrals and show up in the graphs only in the core region. Only for the transfer from Si to Ge are the transferred orbitals generally good approximations to the true valence orbitals as judged by errors of 4% and less in the expectation values of the Fock operator and the kinetic-energy operator. The next best accuracy is attained for P → As, where the errors increase to about 15%. The F^0 integrals, on the other hand, have errors ranging from 0.1% for Si → Ge to 8% for Cl → Br. Clearly for quantitive purposes, valence-shell atomic orbitals are transferrable only for the calculation of integrals, such as F^0, which do not depend strongly on those parts of the valence orbitals which overlap the atomic cores. This is what makes the calculations

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(12) This argument is based on that advanced by M. H. Cohen and V. Heine, *Phys. Rev.*, **122**, 1821 (1961).

(13) One method is that suggested by H. F. King, R. E. Stanton, H. Kim, R. E. Wyatt, and R. G. Parr, *J. Chem. Phys.*, 47, 1936 (1967).

(14) This is a mathematically well-known transformation. A clear presentation of it can be found in Apendix A of P. O. Löwdin, *Phys. Rev.*, **139**, A357 (1965).

Table XVII. Slater Integrals F^0 over s Valence Orbitals for Negative Atomic Ions (au)

	I^a	III (^{3}P)	III (^{1}D)	IV (^{4}S)	IV (^{2}D)	IV (^{2}P)
Row 3	0.16277	0.33266	0.33737	0.39237	0.39548	0.39829
Row 4b	0.15292	0.35046	0.35443	0.39095	0.39371	0.39567
3-4b	0.16207	0.33128	0.33594	0.39030	0.39338	0.39619
	V (^{3}P)	V (^{1}D)	V (^{1}S)	VI	VII	
Row 3	0.45308	0.45454	0.45647	0.51023	0.56555	
Row 4b	0.43248	0.43369	0.43543	0.47061	0.50660	
3-4b	0.45010	0.45155	0.45347	0.50616	0.56019	

^{a} These data are for Li$^-$, Na$^-$, and Li$^- \rightarrow$ Na$^-$.

Table XVIII. Slater Integrals F^0 over p Valence Orbitals for Negative Atomic Ions (au)

	III (^{3}P)	III (^{1}D)	IV (^{4}S)	IV (^{2}D)	IV (^{2}P)
Row 3	0.20494	0.18517	0.28452	0.27254	0.26263
Row 4b	0.20258	0.18415	0.27452	0.26294	0.25433
3-4b	0.20411	0.18441	0.28231	0.27037	0.26149
	V (^{3}P)	V (^{1}D)	V (^{1}S)	VI	VII
Row 3	0.33931	0.33385	0.32658	0.39610	0.45265
Row 4b	0.31580	0.31091	0.30430	0.35692	0.39689
3-4b	0.33511	0.32965	0.32240	0.38923	0.44245

Table XIX. Total Electronic Energies (au) for Negative Atomic Ions

	I^a	III (^{3}P)	III (^{1}D)	IV (^{4}S)	IV (^{2}D)	
Row 4b	−161.855	−1923.260	−1923.239	−2075.394	−2075.347	
3-4b	−161.837	−1923.150	−1923.127	−2075.203	−2075.154	
	IV (^{2}P)	V (^{3}P)	V (^{1}D)	V (^{1}S)	VI	VII
Row 4b	−2075.317	−2234.222	−2234.185	−2234.131	−2399.904	−2572.535
3-4b	−2075.123	−2233.856	−2233.818	−2233.762	−2399.226	−2571.370

^{a} These data are for Na$^-$ and Li$^- \rightarrow$ Na$^-$.

Table XX. First Ionization Potentials (eV) of the Elements in Their Ground States^a

Period	I		II		III		IV		V		VI		VII		VIII	
1	H	13.595													He	24.581
2	Li	5.390	Be	9.320	B	8.296	C	11.256	N	14.53	O	13.614	F	17.418	Ne	21.559
3	Na	5.138	Mg	7.644	Al	5.984	Si	8.149	P	10.484	S	10.357	Cl	13.01	Ar	15.755
4a	K	4.339	Ca	6.111												
4b	Cu	7.724	Zn	9.391	Ga	6.00	Ge	7.88	As	9.81	Se	9.75	Br	11.84	Kr	13.996
5a	Rb	4.176	Sr	5.692												
5b	Ag	7.574	Cd	8.991	In	5.785	Sn	7.342	Sb	8.639	Te	9.01	I	10.54	Se	12.127

^{a} These values were taken from the "American Institute of Physics Handbook," McGraw-Hill Book Co., Inc., New York, N. Y., 1963.

relevant to molecules, as will be discussed at the end of this section.

On the basis of the usual arguments concerning the relative penetration of s and p orbitals into the core regions,[15] one might have expected p orbitals to be more transferable than s orbitals. The calculations in this paper do not show this to be the case generally.

Although the pattern of transferability in the part of the periodic table which has been explored cannot be explained here, it can be correlated with the ionization potentials of the elements. In addition, an indication of why there should be a correlation can be made, and on the basis of these observations other pairs of atoms can be selected, for which the valence-shell orbitals should be transferable. In Table XX are presented the first ionization potentials of a relevant portion of the periodic table. Comparison of this table with Tables II, III, XI, and XII shows that where there are small percentage differences in the ionization potentials of elements in the same column of the periodic table, the valence orbitals will be transferable to some degree. The greatest transferability as determined in the preceding section does not, however, correlate with the smallest percentage differences in the ionization potentials, *i.e.*, the relationship is not one-to-one. However, the correlation is mathematically reasonable.

The correlation is made to be reasonable by recalling that for all closed-shell configurations and a few open-shell configurations, the ionization potential is approximately equal to the eigenvalue of the smallest occupied orbital. In general, the ionization potential is equal approximately to the orbital energy plus correction terms. Recently it has been shown that for large r a radial function will be essentially $\exp(-\sqrt{2|\epsilon|}r)$, where ϵ is the energy of the smallest occupied orbital.[16] In Table XXI the orbital eigenvalues are given for the elements studied. Note that the observed degree of transferability of valence orbitals correlates well with the orbital energies. It thus appears that valence orbitals having equal ϵ's are, outside the core region, nearly equal, which is what one expects for sufficiently

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(15) *Cf.* H. E. White, "Introduction to Atomic Spectra," McGraw-Hill Book Co., Inc., New York, N. Y., 1934, Chapter VII.

(16) N. C. Handy, M. T. Marron, and H. J. Silverstone, *Phys. Rev.*, **180**, 45 (1969).

Table XXI. Neutral Atom Valence Orbital Energies (au) for s Symmetry

Row	I	II	III	IV (^{3}P)	IV (^{1}D)	V (^{4}S)	V (^{2}D)
1	−0.5000						
2	−0.1963	−0.3093	−0.4947	−0.7056	−0.7187	−0.9452	−0.9636
3	−0.1821	−0.2530	−0.3935	−0.5399	−0.5476	−0.6964	−0.7065
4a	−0.1474	−0.1955					
4b	−0.2367	−0.2925	−0.4245	−0.5533	−0.5609	−0.6859	−0.6952

Row	V (^{2}P)	VI (^{3}P)	VI (^{1}D)	VI (^{1}S)	VII	VIII
1						−0.9180
2	−0.9763	−1.2443	−1.2565	−1.2751	−1.5725	−1.9305
3	−0.7134	−0.8796	−0.8859	−0.8957	−1.0731	−1.2775
4a						
4b	−0.7016	−0.8373	−0.8429	−0.8517	−0.9927	−1.1529

Table XXII. Neutral Atom Valence Orbital Energies (au) for p Symmetry

Row	III	IV (^{3}P)	IV (^{1}D)	V (^{4}S)	V (^{2}D)	V (^{2}P)
1						
2	−0.3099	−0.4333	−0.3813	−0.5675	−0.5086	−0.4713
3	−0.2102	−0.2971	−0.2609	−0.3917	−0.3506	−0.3243
4b	−0.2085	−0.2873	−0.2518	−0.3695	−0.3302	−0.3050

Row	VI (^{3}P)	VI (^{1}D)	VI (^{1}S)	VII	VIII
1					
2	−0.6319	−0.6007	−0.5555	−0.7300	−0.8505
3	−0.4374	−0.4154	−0.3835	−0.5065	−0.5912
4b	−0.4028	−0.3822	−0.3524	−0.4571	−0.5241

large r. It is interesting that larger r appears to be r outside the core region. (This does not mean that the orbitals are just $\exp(-\sqrt{2|\epsilon|}r)$ exterior to the core.) Study of Tables XXI and XXII further suggests that if the qualitative mathematical arguments are correct, it might be reasonable to transfer orbitals down and across the periodic table, *e.g.*, from B to Si, from C to P, from O to Cl, but not from N to S or from F to Ar.[17] Figure 9 suggests that for the s orbital of B and Si, the orbital energy is a valid guide, but Figure 10 for the p orbitals does not. Transfer calculations on B to Si, C to P, and O to Cl gave overlap integrals smaller tha 0.99.

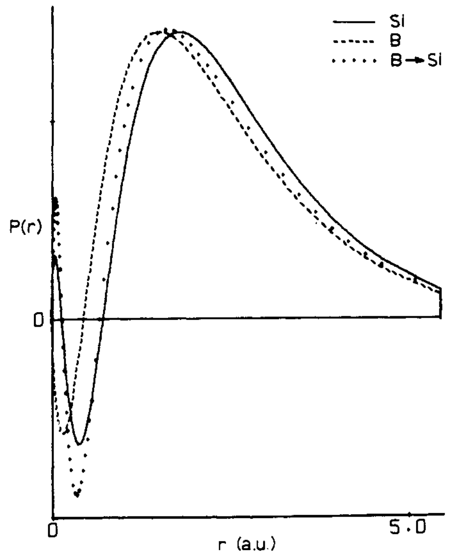

Figure 9. Radial parts of the B 2s and Si 3s Hartree–Fock and the B → Si transfer orbitals.

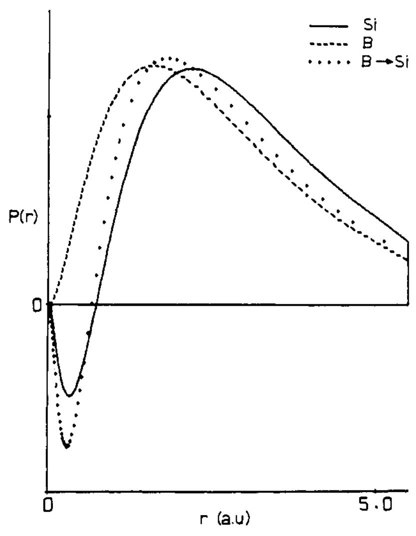

Figure 10. Radial parts of the B 2p and Si 3p Hartree–Fock and the B → Si transfer orbitals.

This study is obviously related to every study which has revealed that there are periodicities in the properties of the elements. Most such studies have dealt with experimentally determined properties or with expectation values of such variables as the radial distance from the nucleus. It should not have been expected that the orbitals would come out to be nearly equal for many pairs of atoms. For example, the valence-shell orbitals of Si are 3s and 3p, and those of Ge 4s and 4p. Certainly 3s and 4s and 3p and 4p orbitals should be different in the way that Slater orbitals of total quantum number 3 and 4 are different. But this study shows that they are

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(17) This is quite reasonable chemically; see F. Ephrain, "Inorganic Chemistry," revised by P. C. L. Thorne and E. R. Roberts, Oliver and Boyd, London, 1954, p 65.

not very different. And that is why they give similar expectation values.

The study most closely related to this one is based on pseudopotentials.[18] That study does not deal with the properties of accurate Hartree–Fock orbitals. The pseudopotential method idea could be used as a partial explanation of the results of this paper; *i.e.*, the valence orbital is primarily determined by regions exterior to the core.[12] Another study related to the present one has recently been published.[19] In that study the potentials seen by orbitals in the Hartree–Fock–Slater approximation have been examined. These potentials, for radial distances larger than one atomic unit, appear to be quite similar in some cases for atoms in the same column of the periodic table, but unfortunately the published graph is too small to be interpreted with accuracy. If the potentials are the same, then obviously the orbitals should be the same. However, if the potentials are the same except in the core region, then the question becomes why are they the same.

Up to this point the question of the transferability of atomic valence-shell orbitals has been discussed as if it were primarily relevant to atomic properties. In fact its real relevance is to molecular properties and, in particular, to the question of the transferability of localized orbitals between molecules.[2,20] This question is regarded by some theorists as a key question in the quantative understanding of chemistry through quantum mechanics. The following paragraphs sketch some of the arguments that relate the atomic calculations to the molecular problem and point out how the atomic calculations will influence the molecular studies which are beginning in this laboratory.

The most direct way to see that there should be a correspondence between the atomic transferability calculations and the transferability of localized orbitals is to consider a series of simple examples. Suppose one has settled on a suitable definition for the localized orbital of H^- in LiH and NaH.[21] One must expect that the H^- orbital from LiH will differ from that from NaH even when the nuclear separation is R in both molecules. The H^- orbital is transferable from LiH to NaH if it can be used, to a desired degree of accuracy, in place of the H^- orbital of NaH in the calculation of a selected set of properties of NaH. If the separation between the nuclei in both molecules is decreased from R to $R - \Delta R$, the effect in both cases is to increase the overlap between the negative- and positive-ion charge densities. Thus the H^- orbital in each case is acted on more strongly by the core part of the positive ion as a result of the decrease in R, and it is in that part of the H^- orbitals which overlaps the core region of the positive ions that the two H^- orbitals should differ most. (This picture is consistent with the atomic calculations.) Outside the core region of the positive ion, both Li^+ and Na^+ are the sources of essentially the same potential, that due to a single positive charge.[22] Thus as R decreases, it is *plausible* that the transferability of the H^- orbital from LiH to NaH should decrease. In the limit of the united atom LiH becomes Be and NaH becomes Mg. The H^- orbital becomes in Be, the 2s orbital, and in Mg, the 3s orbital. If the 2s orbital were *accurately* transferable from Be to Mg, then one would expect the H^- orbital of LiH to be transferable to NaH at a given R value. This is one of the considerations that initiated the study described in this paper.

The arguments of the preceding paragraph can be extended in various ways. For example, are the F^- orbitals transferable from LiF to NaF when the nuclear separation in both is R? First one should eliminate the F^- $(1s)^2$ core by a localized orbital type transformation,[23] then consider the limit of $R = 0$. In this case LiF becomes Ne and NaF becomes Ar. If the valence-shell orbitals of Ne are *accurately* transferable to Ar, then one might expect the F^- localized orbitals to be accurately transferable from LiF to NaF. In a similar fashion one can go on to consider other cases in which the localized orbitals of an atom, ion, or radical X in the molecule AX are transferred to a molecule BX. In more chemical language, the question being asked is: what is the effect on the orbitals of X in a molecule if B is substituted for A?

It should now be clear that the studies herein described of the transferability of valence-shell atomic orbitals provide a map of the periodic table which tells one for which substitutions of atoms the localized orbitals of the remainder of a molecule are most likely to be changed and for which they are least likely to be changed. Thus when molecular transferability tests are made, they may, in light of the atomic calculations, make it plausible that localized orbitals are never transferable to a useful degree of accuracy, or that they are generally transferable. Most likely, molecular calculations will show the true situation to lie between the extremes. The atomic calculations will still play the role of a map. Programs to carry out molecular studies using nonorthogonal localized orbitals are being written here, and should be running before this article appears in print.[24]

It is possible to go a step further and argue that the atomic calculations have made it highly probable that for certain favorable cases, *e.g.*, Si → Ge, the substitution of one congener for another should have a small effect on the electronic total energy, and that accurate molecular orbitals might be derived from transferred localized orbitals. If the molecular orbitals are localized onto atoms, then the localized orbitals should be large about each atom and contain small distortions about neighboring nuclei.[25] For the sake of argument, suppose that the contribution to a localized orbital from the core region about a neighboring atom A accounts for 0.1 electronic charge. Also, suppose that the atomic calculations show that substitution of atom B for atom A leads to a 50% error in some matrix element

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[18] B. J. Austin and V. Heine, *J. Chem. Phys.*, **45**, 928 (1966).

[19] A. R. P. Rau and V. Fano, *Phys. Rev.*, 167, 7 (1968).

[20] C. Edmiston and K. Ruedenberg, *J. Chem. Phys.*, **43**, S97 (1965).

[21] Reference 2 contains a rather complete list of suggested methods of defining and calculating localized orbitals.

[22] It is possible to derive equations from which localized orbitals can be calculated without first calculating molecular orbitals. The effective potentials appearing in these equations are made up of local coulombic potentials, and nonlocal potentials. Overlap corrections are present in each potential. The most recent proposal of this sort is by D. Peters, *ibid.*, 51, 1559 (1969). *Cf.* ref 2 and W. H. Adams, *ibid.*, 37, 2009 (1962).

[23] See the references cited in footnote 21.

[24] The calculations of Edmiston and Ruedenberg show that the orthonormal *equivalent orbitals* are generally not transferable (see footnote 20.) The nonorthogonal localized orbitals which have been suggested here should be more transferable for the reasons given in ref 2.

[25] Preliminary localized orbital analysis of HeNe, LiF, and NaCl according to the scheme of ref 2 have shown their distortion relative to isolated atoms and ions to be quite small.

in the atomic calculations. One might expect then that, in two molecules which differ only in the substitution of B for A, the localized orbitals of the rest of the molecule containing A could be used to calculate the corresponding molecular matrix element with an error of the order of magnitude of 5%; *i.e.*, the 50% error in the atomic case is weighted by the contributions of the A and B atomic core regions to the localized orbital. Thus, although atomic transferability as tested in this paper is shown not to be an accurate method for approximating atomic orbitals, localized orbitals may be transferable to a useful accuracy; but that can be demonstrated only by direct calculation.

If one assumes that localized orbitals for some kinds of molecules will be transferable to a useful degree of accuracy, one is led to consider the physical consequences of the transferability. For example, one should consider the possibility that the potential surfaces of these molecules may be interrelated except for core contributions. To be more specific, if the H^- orbital is transferable in the case of LiH and NaH, one might expect that the potential curves of each at identical nuclear separations will differ primarily due to the differences between the Li^+ and Na^+ ions, differences which should become pronounced only as the hydrogen nucleus penetrates into the Li and Na core regions. If this is the case, can the corrections be introduced without resort to full electronic calculations? Clearly these are not the only speculations one can make if one assumes that there are transferable localized orbitals; but it is also clear that the next step needed is molecular transferability calculations, not extensive speculations.

Conclusions

One general conclusion to be drawn from this study is that *ab initio* Hartree–Fock valence atomic orbitals have properties consistent with the idea of chemical periodicity. This is a very interesting result since these orbitals contain no adjustable parameters on which one might build in the periodicity. The periodicity is a consequence of the quantum mechanical equations. Some implications of this have been discussed. In addition to this general conclusion, the following specific conclusions may be drawn from the calculations.

The atomic valence-shell Hartree–Fock orbitals of congeners are generally about the same size and in some cases are nearly identical except in the atomic core region. The differences in the core region when two valence orbitals are nearly identical outside of the core seem to be due primarily to the valence orbitals being orthogonal to different core orbitals. The accuracy to which the valence-shell orbitals of one atom approximate those of another depends upon the energies of the valence orbitals of each symmetry being nearly equal for the two atoms. This means that the valence-shell orbitals of two atoms may be nearly identical even though they are not congeners. The use of the valence-shell orbitals of one atom as approximations to the valence-shell orbitals of another atom is not justified in the calculation of most energy integrals. The Slater two-electron integrals can be approximated in this way with errors of less than 10% for transfers of valence orbitals from third- to fourth-period congeners in columns III through VI.

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Theoretical Band Shapes for Vibronically Induced Electronic Transitions

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Abstract: Intensity distributions associated with vibronically induced electronic transitions are calculated by a method in which the vibrational wave functions of both the initial and final electronic states are expanded in a truncated basis of harmonic oscillator eigenstates. Results are given for transitions between harmonic oscillators with different force constants, between harmonic oscillators with different equilibrium positions, and between a harmonic oscillator and a double-minimum well. The distributions are characterized by their spectral moments and by bar-graph plots of the spectra. Comparisons are made to the corresponding Franck–Condon distributions for an allowed transition, showing differences that might serve as evidence for a vibronic intensity mechanism in an experimental spectrum.

In the analysis of absorption band shapes of electronic transitions thought to be vibronically induced a simplifying assumption is often made, namely that the intensity distribution with respect to the vibronically active mode consists at 0°K of but a single line, this $0 \rightarrow 1$ transition being in effect a false origin upon which are built normal Franck–Condon distributions with respect to the remaining modes, including the totally symmetric vibration. At higher temperatures there would be two origins, corresponding to $\Delta v = \pm 1$, where