Calculations on the Electronic Spectra of trans-*Butadiene by a Semi-empirical Molecular-orbital Approximation.*

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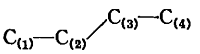
Calculations on the lowest electronic transitions of *trans*-butadiene have been carried out within the framework of a semi-empirical molecular-orbital approximation recently proposed by Pariser and Parr. The " best " possible wave functions for the molecule predict values of the energy and intensity of transitions that are in satisfactory agreement with experimental results. The problem of choosing the most significant configurations to build a good, approximate wave function is discussed. Finally, a comparison is made between the use of arbitrary molecular orbitals and self-consistent field (SCF) molecular orbitals as the starting point for the calculations.

One of the interesting possibilities for the use of a semi-empirical molecular-orbital approximation recently proposed by Pariser and Parr (*J. Chem. Phys.*, 1953, **21**, 466, 767; cf. Pople, *Trans. Faraday Soc.*, 1953, **49**, 1375) appears to be in the study of the molecular properties of large molecules in a more satisfactory manner than has yet been possible. Heretofore, there has been only a very limited application of the non-empirical antisymmetrized molecular orbital (ASMO) approximation, including configuration interaction (CI), to molecules of even moderate size such as naphthalene (*e.g.*, Jacobs, *Proc. Phys. Soc.*, 1948, **62**, *A*, 710). This has been largely due to the very tedious algebra necessary in calculations of the matrix elements, although it is now likely that electronic computers could aid in avoiding a considerable portion of the labour. For the smaller molecules, for which it has been possible to construct the best possible wave functions within the framework of the non-empircal ASMO–CI approximation, the accord between the predictions of the calculations and the experimental observations on electronic spectra often leaves much to be desired. The order of excited levels may not be the same, or, in those cases where there is agreement as to the order, the calculated and the observed transition energies may differ by several electron-volts.

The results published so far (Pariser and Parr, *loc. cit.*) on the application of the semi-empirical approximation to some hydrocarbons and heteromolecules give satisfactory agreement between calculation and experiment, although for each example wave functions have been built from a superposition of only a few of the total possible number of configurations. Before one can definitely assess the value of this approximation, it will be necessary to consider one molecule in rather greater detail than has been done up to now.

Pariser and Parr have reported partial calculations on butadiene (utilizing 3 of the possible 12 configurations for the ground state, and 2 of the possible 8 configurations for the excited state) and the accord between experiment and calculation on the energy and order of electronic transitions is satisfactory. As a model and guide to calculations for large molecules we now expand these calculations. Specifically, we shall be interested in four aspects of the calculations on ultra-violet spectra : (1) Using the ASMO non-empirical approximation and starting either with Hückel or SCF orbitals, single configuration calculations on the electronic spectra of butadiene are in qualitative agreement with the observed order of transition (*i.e.*, an allowed transition followed by a forbidden transition) although the predicted energies are 2—3 ev larger than the excitations observed. However, when nearly the " best " possible wave functions, obtained from the CI procedure, are used, the order of calculated transition changes so that the forbidden should be of lower energy than the allowed transition (Lefebvre, Ph.D. Thesis, London, 1953; Pullman and Baudet, *Compt. rend.*, 1954, **238**, 241). It will be of interest to know whether a similar crossing of the lowest excited levels occurs in this semi-empirical approximation when the " best " wave functions are used. (2) The identification of transitions will be more secure if a quantitative comparison of observed and calculated intensities is made in addition to a comparison of transition energies. Pariser and Parr's calculations give no information on this point. (3) Even by using an electronic calculator it will, in general, for the larger molecules, not be possible to build up the state wave functions from all possible configurations. We shall discuss some arbitrary methods of choosing the most important configurations. (4) Linked with (3) is the difficult problem of choosing the set of molecular orbitals with which to commence calculation. To illustrate this point, a comparison will be made between an arbitrary set of orbitals and the SCF molecular orbitals, which are found within the framework of the semi-empirical approximation.

Calculations.—The details of the method of calculation have been given by Pariser and Parr. *trans*-Butadiene will be assumed to have the following form :



with $C_{(1)}$–$C_{(2)} = 1{\cdot}35$ Å, $C_{(2)}$–$C_{(3)} = 1{\cdot}46$ Å, and $\angle C_{(1)}C_{(2)}C_{(3)} = 124°$ (Shomaker and Pauling, *J. Amer. Chem. Soc.*, 1939, **61**, 1769) : it is, of course, planar. Only the four $2p\pi$ electrons will be considered explicitly; the $2p\sigma$ electrons are considered only as they furnish a potential field in which the π electrons move. For the four electrons four molecular orbitals can be written, and the orthonormal set suggested by Parr and Pariser will be used. In order of increasing energy, they are :

$$\begin{array}{llc} & & \text{Symmetry} \\ & & \text{(point group } C_{2h}\text{)} \\ \phi_K & = \tfrac{1}{2}(\chi_1 + \chi_2 + \chi_3 + \chi_4) & a_u \\ \phi_L & = \tfrac{1}{2}(\chi_1 + \chi_2 - \chi_3 - \chi_4) & b_g \\ \phi_M & = \tfrac{1}{2}(\chi_1 - \chi_2 - \chi_3 + \chi_4) & a_u \\ \phi_N & = \tfrac{1}{2}(\chi_1 - \chi_2 + \chi_3 - \chi_4) & b_g \end{array} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The symmetry symbols of lower-case letters refer to the symmetry of the individual molecular orbitals; the symmetry symbols of capital letters refer to the symmetry of configurations. It may be well to recall that $a_u \times b_g = B_u$, $a_u \times a_u = A_g$, and $b_g \times b_g = A_g$.

These particular molecular orbitals have been chosen in this instance because they are convenient mathematically. As the state functions will be built from a linear combination of " all possible " configurations, algebraic convenience is sufficient reason. Pariser and Parr pointed out that these orbitals would probably be close to the SCF orbitals and that is, in fact, so (see below).

By distributing the four electrons in the four molecular orbitals it would be possible to write 70 independent wave functions. The problem will be simplified by considering only the singlet states, as the triplet state of butadiene does not appear, as yet, to have been accurately observed.

It will be desirable to have a simple notation to indicate the space co-ordinates of the configurations. For example, K^2L^2 will indicate the configuration in which there are two electrons in ϕ_K and two in ϕ_L. The determinantal wave function can be written as :

$$\psi_{K^2L^2} = (4\,!)^{-\frac{1}{2}} \det.|\phi_K(1)\alpha(1)\ \phi_K(2)\beta(2)\ \phi_L(3)\alpha(3)\ \phi_L(4)\beta(4)| \equiv |\phi_K\bar{\phi}_K\phi_L\bar{\phi}_L| \quad . \quad (2)$$

For one electron in each of two molecular orbitals, either a singlet or triplet can be written and only the former will be considered here:

$$\psi_{K^2LM} = (2)^{-\frac{1}{2}}\{|\phi_K\bar{\phi}_K\phi_L\bar{\phi}_M| - |\phi_K\bar{\phi}_K\bar{\phi}_L\phi_M|\} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

When there is one electron in each of the four molecular orbitals some difficulty will arise, for then two singlets can be written for this distribution. If these are taken to be of the same form as Coulson and Jacobs (*Proc. Roy. Soc.*, 1951, *A*, **206**, 281) used for butadiene:

$$\psi^a{}_{KLMN} = \tfrac{1}{2}\{|\phi_K\bar{\phi}_L\phi_M\bar{\phi}_N| - |\bar{\phi}_K\phi_L\phi_M\bar{\phi}_N| - |\phi_K\bar{\phi}_L\bar{\phi}_M\phi_N| + |\bar{\phi}_K\phi_L\bar{\phi}_M\phi_N|\} \quad . \quad (4)$$

$$\psi^b{}_{KLMN} = \tfrac{1}{2}\{|\phi_K\bar{\phi}_L\phi_M\bar{\phi}_N| - |\phi_K\phi_L\bar{\phi}_M\bar{\phi}_N| - |\bar{\phi}_K\bar{\phi}_L\phi_M\phi_N| + |\bar{\phi}_K\phi_L\bar{\phi}_M\phi_N|\} \quad . \quad (5)$$

it will be observed that expressions (4) and (5) are not orthogonal. It will be convenient to take the following linear combinations that are:

$$\psi^A{}_{KLMN} = (\psi^a{}_{KLMN} + \psi^b{}_{KLMN})/\sqrt{3} \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$$\psi^B{}_{KLMN} = (\psi^a{}_{KLMN} - \psi^b{}_{KLMN}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

In only one unimportant detail do the calculations reported here differ from those carried out by Pariser and Parr. Here, all effect of the hydrogen atoms in the molecule will be ignored. In substance, this results in a change of their formula for α_p to:

$$\alpha_p = W_{2p} - \sum_{p \neq q}[(pp|qq) + (q:pp)] \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where the notation is that used by Pariser and Parr. This has been done to make more meaningful a comparison between these calculations and non-empirical ASMO–CI calculations where all effect of the hydrogen atoms was neglected. It will now be necessary to give an explicit value to $(q:pp)$, which has been assumed to have an average value of 0·6 ev for nearest neighbours and 0·1 ev for next-nearest neighbours. The value of $(q:pp)$ for $C_{(1)}$–$C_{(2)}$ should, of course, be somewhat larger than for $C_{(2)}$–$C_{(3)}$, but it will probably introduce only a negligible error in the calculation to take an average value. The values of other atomic integrals have been given by Pariser and Parr. It should be mentioned that whether one calculates α as Pariser and Parr have done or by equation (8), it will not affect the value of the empirical parameters β or the diagonal elements of the matrix; it will, however, make some difference in a few of the non-diagonal elements.

Within the framework of this semi-empirical approximation it is possible to calculate the SCF molecular-orbitals for butadiene. Pople (*loc. cit.*) has given the general formulæ for the calculation of the eigenfunctions of the Hartree–Fock operator (cf. Roothann, *Rev. Modern Phys.*, 1951, **23**, 69; Parr and Mulliken, *J. Chem. Phys.*, 1950, **18**, 1338; Coulson and Jacobs, *loc. cit.*) and has calculated the orbitals for the ground state of butadiene for a semi-empirical approximation similar to that used in this paper. The exact value of the orbitals will depend on the precise details of the computation. The equations (9) differ slightly from those given by Pople:

$$\left.\begin{aligned}\phi_k &= 0{\cdot}426(\chi_1 + \chi_4) + 0{\cdot}564(\chi_2 + \chi_3)\\ \phi_l &= 0{\cdot}536(\chi_1 - \chi_4) + 0{\cdot}461(\chi_2 - \chi_3)\\ \phi_m &= 0{\cdot}564(\chi_1 + \chi_4) - 0{\cdot}426(\chi_2 + \chi_3)\\ \phi_n &= 0{\cdot}461(\chi_1 - \chi_4) - 0{\cdot}536(\chi_2 - \chi_3)\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

To distinguish these SCF molecular orbitals from the arbitrary molecular orbitals used in expression (1), lower-case indices *k, l, m, n* are used here.

The results of the calculations are gathered in the several tables. In Table 1 the data for the wave function for the ^1A_g state that can be obtained from a consideration of all possible configurations of this symmetry have been summarized. In columns (*a*) are listed the space co-ordinates of the configurations, in (*b*) the energy of the configurations relative to the lowest configuration before CI, in (*c*) the energy of the one or two lowest configurations after CI, in (*d*) the weight, *i.e.*, the square of the coefficient, of that configuration in the total wave function, and in (*e*) the lowering of the lowest configuration by the configuration in question calculated by second-order perturbation theory. This has been done by the usual formula:

$$H_{oi}^2/(H_{ii} - H_{oo}) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (10)$$

where the index o refers to the lowest configuration and i refers to any other configuration. The starting molecular orbitals for the calculations of this and the next four Tables have been the functions (1).

Table 2 lists similar data for the eight possible configurations in the ^1B_u state.

In Table 1 it will be observed that there are three configurations for which the second-order perturbation theory gives a lowering of zero, which is to say that as a first approximation the effect of these configurations in the total wave function should be very small. In Table 3 are collected the data for the ^1A_g state when only the nine mono- and di-excited configurations are considered as contributing to the wave function.

Tables 4 and 5 are more restrictive, considering only the mono-excited configurations as making a contribution to the ^1A_g and the ^1B_u state respectively.

TABLE 1. ^1A_g *state of butadiene* (12 *configurations*).

(*a*)	(*b*) (ev)	(*c*) (ev)	(*d*)	(*e*) (ev)
K^2L^2	0·00	−0·77	0·927	—
K^2M^2	10·24	—	0·010	0·056
K^2N^2	13·70	—	0·003	0·049
L^2M^2	13·70	—	0·002	0·049
L^2N^2	16·96	—	0·002	0·034
M^2N^2	23·36	—	0·000	0·000
KL^2M	7·67	+6·50	0·035	0·337
KMN^2	19·35	—	0·000	0·000
K^2LN	7·67	—	0·004	0·075
LM^2N	19·35	—	0·000	0·000
$KLMN^A$	16·14	—	0·011	0·107
$KLMN^B$	14·32	—	0·006	0·053
			Total	0·76

TABLE 2. ^1B_u *state of butadiene* (8 *configurations*.)

(*a*)	(*b*) (ev)	(*c*) (ev)	(*d*)	(*e*) (ev)
K^2LM	5·88	5·68	0·967	—
LMN^2	20·92	—	0·003	0·038
L^2MN	17·11	—	0·000	0·016
K^2MN	12·07	—	0·002	0·002
KLM^2	13·75	—	0·009	0·064
KLN^2	17·11	—	0·002	0·016
KL^2N	9·25	—	0·012	0·020
KM^2N	17·56	—	0·004	0·043
			Total	0·199

TABLE 3. ^1A_g *state of butadiene* (9 configurations).

(*a*)	(*b*) (ev)	(*c*) (ev)	(*d*)	(*e*) (ev)
K^2L^2	0·00	−0·76	0·929	—
K^2M^2	10·24	—	0·009	0·056
K^2N^2	13·70	—	0·003	0·049
L^2M^2	13·70	—	0·002	0·049
L^2N^2	16·96	—	0·002	0·034
KL^2M	7·67	+6·58	0·035	0·337
K^2LN	7·67	—	0·005	0·075
$KLMN^A$	16·14	—	0·010	0·107
$KLMN^B$	14·32	—	0·005	0·053
			Total	0·76

TABLE 4. ^1A_g *state of butadiene* (3 *configurations*).

(*a*)	(*b*) (ev)	(*c*) (ev)	(*d*)	(*e*) (ev)
K^2L^2	0·00	−0·39	0·955	—
KL^2M	7·67	7·55	0·038	0·337
K^2LN	7·67	—	0·008	0·075
			Total	0·412

TABLE 5. ^1B_u *state of butadiene* (3 *configurations*).

(*a*)	(*b*) (ev)	(*c*) (ev)	(*d*)	(*e*) (ev)
K^2LM	5·88	5·81	0·990	—
KLM^2	13·75	—	0·010	0·064
K^2MN	12·07	—	0·001	0·002
			Total	0·066

(For meanings of *a*—*e* see text.)

There would be no point in calculating the best wave functions using the SCF orbitals (9) as the result would, of course, be the same as that previously found. It has been thought of interest to calculate the relative energies of the configurations and the approximate lowering of the lowest configuration as calculated by second-order perturbation theory. These results are collected in Tables 6 and 7 for the ^1A_g and the ^1B_u state respectively.

TABLE 6. ^1A_g *state of butadiene (calculated from SCF orbitals).*

(*a*)	(*b*) (ev)	(*e*) (ev)	(*a*)	(*b*) (ev)	(*e*) (ev)	(*a*)	(*b*) (ev)	(*e*) (ev)
k^2l^2	0·00	—	l^2n^2	17·12	0·024	$klmn^A$	16·51	0·082
k^2m^2	10·73	0·095	kl^2m	7·85	0·000	$klmn^B$	14·56	0·051
k^2n^2	13·84	0·046	k^2ln	7·68	0·000			
l^2m^2	14·46	0·039					Total	0·337

TABLE 7. ^1B_u *state of butadiene (calculated from SCF orbitals for* ^1A_g *state).*

(*a*)	(*b*) (ev)	(*e*) (ev)	(*a*)	(*b*) (ev)	(*e*) (ev)	(*a*)	(*b*) (ev)	(*e*) (ev)
k^2lm	6·39	—	k^2mn	13·98	0·017	kl^2n	9·23	0·040
lmn^2	21·74	0·028	klm^2	14·19	0·051	km^2n	18·18	0·028
l^2mn	17·49	0·029	kln^2	17·08	0·000			
							Total	0·193

Discussion.—In Table 8 are summarized the data on the electronic spectra. In column (*a*) are the experimental results; other columns give the results of calculations using (*b*) the best wave functions of Tables 1 and 2, (*c*) the approximate function of Table 3 for the ^1A_g state, (*d*) the mono-excited configurations of Tables 4 and 5, (*e*) the lowest configurations [starting with equations (1)], (*f*) the lowest configurations starting with the SCF orbitals (9), and (*g*) the lowest configurations starting with the non-empirical SCF orbitals; for (*h*) calculations were used similar to those for (*c*) in the ASMO–CI approximation.

The *f* values in (*a*)—(*f*) have been calculated by using the computed value of the excitation energy. For consistency with the fundamental assumptions of the approximation, all cross-terms have been neglected. In (*g*) and (*h*) it is not clear what value (computed or experimental) of the transition energy has been used.

First, it is observed that the agreement between (*a*) and (*b*) is very satisfactory. This suggests that if it were possible to use the best wave functions in this semi-empirical scheme, the value of the predictions should be reasonably significant. Unfortunately, in practice it will not be possible to construct the best wave functions for large molecules even by using an electronic computer. It will always be necessary to attempt to choose the most significant configurations so as to approximate satisfactorily to the best wave function. Some possible approximations are columns (*c*)—(*f*). The agreement between (*a*) and (*c*) is also satisfactory, and the difference between (*b*) and (*c*) is not very large. If it should be generally true that one can neglect all configurations which differ from the lowest configuration by more than two orbitals, then the enormously tedious problem of CI would be reduced to a scale that an electronic computer might be able to handle in a fairly complete manner. The three configurations in Table 1 for which the second-order perturbation-theory lowering is zero might have been excluded from the calculation on the grounds that the energies of these configurations are so high (~20 ev above the lowest configuration) that the whole approximation of CI breaks down. Whether one is justified in doing this depends somewhat on whether one thinks of CI as being a purely mathematical procedure or whether one assumes that the configurations must have some physical reality, at least to the extent of not appearing in the continuum.

The comparison between (*a*), (*c*), and (*h*) is interesting for here one observes how slightly reliable even very detailed non-empirical calculations can be. The reasons for this are not entirely clear at present, but at least some of the contributing factors are understood. Briefly, the calculated value of the one-centre, two-electron atomic integral is much too large (Moffitt, *Proc. Roy. Soc.*, 1950, *A*, **202**, 534; Pariser, *J. Chem. Phys.*, 1953, **21**, 568) and it seems likely other Coulomb integrals calculated from Slater-type functions are somewhat too large (Pariser and Parr, *loc. cit.*). One cannot follow Pullman and Baudet (*loc. cit.*) in suggesting that the difficulty in butadiene is due to the poor approximation to the ^1B_u wave function. As they included all eight configurations in this calculation, they arrived of necessity at the " best possible " wave function for this state.

The good agreement between (*a*) and (*d*) suggests at first sight that it might be possible to use the lowest configuration and just mono-excited configurations to build a reasonably satisfactory wave function. This possibility, however, needs to be examined with caution. It can be shown (Lefebvre, *Compt. rend.*, 1953, **237**, 1158) that, if one builds configurations from the SCF orbitals for that particular state, the matrix elements between the lowest configuration and mono-excited configurations are zero, while the matrix elements between the lowest configuration and di-excited configurations are not zero. However, if the configurations are constructed from orbitals other than the SCF orbitals, both these matrix elements are usually non-zero and experience in this semi-empirical approximation seems to indicate that the lowering of the lowest configuration by mono-excited configurations (as calculated by second-order perturbation theory) is likely to be greater than that by the di-excited configurations. In a sense, then, the mono-excited are " more important " than the di-excited configurations. One would prefer, of course, to build the wave functions for states from all the important mono- and di-excited configurations, or, alternatively, to start from the SCF orbitals and use the important di-excited configurations. Both these objectives will, unfortunately, be impracticable for many molecules. In such instances, using just the lowest plus mono-excited configurations may lead to a fairly good approximate wave function, though possibly not one better than would have resulted from building only single configurations from the SCF orbitals.

The agreement between (*a*) and (*e*) in Table 8 is also good, but this, particularly with regard to the *f* values, must be considered somewhat fortuitous. The agreement between (*a*) and (*f*) is satisfactory as regards order and energy of transitions but, unfortunately, the calculated intensity is nearly twice that observed. This is disappointing, for the SCF orbitals in this approximation (at least for the ground state) are not difficult to calculate, and, if single configuration calculation had given good agreement for both energy and intensity, much of the difficulty associated with wave-mechanical calculations might have been avoided.

TABLE 8. *Electronic transition energies* (ev) *for* trans-*butadiene.*

Transition :	(*a*)[1]	(*b*)	(*c*)	(*d*)	(*e*)	(*f*)	(*g*)[2, 3]	(*h*)[2, 3]
$^1A_g \longrightarrow {}^1B_u$ ...	6·0	6·45	6·44	6·20	5·88	6·39	8·1	9·6
f value	0·53	0·51	0·51	0·51	0·47	0·93	1·05	0·44
$^1A_g \longrightarrow {}^1A_g$ ...	7·2	7·27	7·34	7·94	7·67	7·68	10·1	7·1

[1] Mulliken, *Rev. Modern Phys.*, 1942, **14**, 265. [2] Lefebvre, *loc. cit.* [3] Pullman and Baudet, *loc. cit.*

The rather large difference in the calculated *f* values of (*e*) and (*f*), while the energies calculated are not very different, is expected. It is well known that *f* values are extremely sensitive to the form of the wave function and, although (1) and (9) are reasonably close together, the small difference between these would be magnified in the calculated *f* values. It is also well known that the energies associated with rather different wave functions may not differ very much. It might be tempting to suppose that the satisfactory qualities of the arbitrary molecular orbitals (1) have some general applicability. The same general form of the orbitals (1) have been applied to calculations on naphthalene, and the resulting configurations do not separate nearly as well as those reported here for butadiene. We hope to present some details of these calculations later.

It is now well known that the SCF single configuration is not an exact eigenfunction of the many-electron Hamiltonian, as with a single configuration one has as yet to account for the energy of correlation of electrons of opposite spin. Lefebvre (*loc. cit.*) has made a careful study of this for butadiene in the ASMO–CI approximation, using the SCF orbitals for the ^1A_g state, and has found that the energy of correlation is fairly considerable, about 2·2 ev. As will be observed from Table 6 this energy is approximated by second-order perturbation theory, which we have seen is likely to be reasonably accurate from Tables 1—5 and to be about 0·3 ev. It appears that the lowering from the analytically computed value of most of the coulomb-type atomic integrals has to a large extent accounted for the correlation energy.

Most of the conclusions that we have reached from studying Tables 1—5 are due to the coincidence that the orbitals (1) are reasonably close to the SCF orbitals (9). From this it has followed that, by the assumptions of this semi-empirical approximation, the configurations are very largely independent of one another. CI is not of primary importance, as in the ASMO–CI approximation, and second-order perturbation theory affords a reasonably good approximation. The emergence of the independenc of configurations may well prove to be one of the most important advantages of the present theory (these advantages are also to be found in Moffitts's theory of "atoms in molecules," *Proc. Roy. Soc.*, 1951, *A*, **210**, 245, and later papers, although it does not now seem likely that this theory can be applied in practice to very large molecules). It may be well to emphasize that this independence probably does not hold if the starting orbitals are very far from the SCF orbitals.

The eigenvalues and eigenvectors of the CI matrices (with the exception of Tables 6 and 7) were determined on ACE at the National Physical Laboratory, Teddington, through the kind co-operation of Dr. J. H. Wilkinson. The author is pleased to acknowledge his indebtedness to Dr. Roland Lefebvre for many stimulating discussions and to Dr. R. Daudel for reading the manuscript. This work has been supported by a grant from the U.S. Public Health Service.

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