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# Continuous Absorption Coefficient of the Hydrogen and Lithium Negative Ions*

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Previous calculations of the continuous absorption coefficient of H$^-$ were based on the use of ground state wave functions obtained through the Ritz variational method. Such functions, although giving good values for the energy, are not in general adequate for the determination of the dipole matrix element needed for the absorption coefficient. Initial and final state functions are constructed for which the following necessary conditions on the true wave functions are satisfied: (1) equality of dipole length, velocity, and acceleration matrix elements and (2) the $\langle r^2\rangle_{\text{Av}}$ and $f$ sum rules. The constructed ground state function is also shown to be reasonable on the basis of energy minimization. The resulting absorption coefficient for H$^-$ is in substantial agreement with the best previously calculated curves and with experiment. The curve for Li$^-$ is also obtained.

## I. INTRODUCTION

THE theoretical evaluation of the continuous absorption coefficient of H$^-$ has long been of great astrophysical interest. Since there is only one bound state, the atomic absorption coefficient is identical to the cross section for photodetachment of an electron. The latter process has recently been investigated in the laboratory.[1]

There have been numerous calculations of this coefficient, the most improved being those of Chandrasekhar.[2–9] All of these calculations have made use of ground state wave functions which have been found to give minimum energy in the Ritz variational procedure. The final state wave function has generally been taken to be a symmetrized product of the hydrogen atom ground state function and a plane wave. It is quite clear[7] that the magnitude of the absorption coefficient, particularly in the visible and infrared, is extremely sensitive to the choice of ground state wave function. It is seen that the use of a many-parameter ground state function which may lower the best previously obtained energy by about 0.1% may cause a corresponding change in the absorption coefficient of as much as 100% over a large range of wavelengths. This emphasizes the fact, which is generally realized, that although one obtains a very good value for the energy in a variational calculation, the resulting wave function can be extremely poor for the calculation of other atomic properties. This will be particularly true for those properties which depend on the correctness of the wave function at relatively large distances from the nucleus. To attempt to overcome this difficulty, Chandrasekhar[8,9] determined the continuous absorption coefficient using the dipole velocity operator. This has the effect of weighting the bound wave function more heavily at smaller distances from the nucleus, where the variational functions are more accurate.

In the present paper we will adopt a different approach to this problem. Wave functions for the ground and continuum states are constructed so that they will satisfy certain necessary conditions, other than energy minimization, which are required of the true wave functions. As an additional test of our constructed ground state function, a variational calculation is performed using a trial function of the same form.

## II. CALCULATION OF ABSORPTION COEFFICIENT

The standard formula obtained from perturbation theory for the atomic absorption coefficient for radiation of frequency $\nu$, in which an electron with velocity $v_i$ is ejected in the $Z$ direction and the atom is left in the $i$th excited state, is

$$\kappa_{\nu i}=\frac{2}{3}\frac{h}{e^2c}\nu v_i|\mu_{zi}|^2. \tag{1}$$

The total absorption coefficient is then $\kappa_\nu=\sum_i\kappa_{\nu i}$, where the sum extends over all energetically possible states. We shall employ the atomic units for length (Bohr radius) and energy (2 Rydberg units) throughout. For a two-electron atomic system the dipole matrix element has the form

$$\mu_{zi}=\int\int\Psi_d^*(z_1+z_2)\Psi_{ci}d\tau_1d\tau_2, \tag{2}$$

in which the discrete and continuum wave functions are solutions of the Schrödinger equation

$$\left\{\nabla_1^2+\nabla_2^2+2\left(E+\frac{1}{r_1}+\frac{1}{r_2}-\frac{1}{r_{12}}\right)\right\}\Psi(\mathbf{r}_1,\mathbf{r}_2)=0. \tag{3}$$

Chandrasekhar[8] has pointed out that when $\Psi_d$ and $\Psi_{ci}$ are exact solutions of Eq. (3), $\mu_{zi}$ may be also

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[2] C. K. Jen, Phys. Rev. **43**, 540 (1933).

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[6] L. R. Henrich, Astrophys. J. **99**, 59 (1943).

[7] S. Chandrasekhar, Revs. Modern Phys. **16**, 301 (1944); Astrophys. J. **100**, 176 (1945).

[8] S. Chandrasekhar, Astrophys. J. **102**, 223 (1945).

[9] S. Chandrasekhar, Astrophys. J. **102**, 395 (1945).

written as the so-called dipole velocity and acceleration matrix elements,

$$-\frac{1}{E_d-E_c}\int\int\Psi_d^*\left(\frac{\partial}{\partial z_1}+\frac{\partial}{\partial z_2}\right)\Psi_{ci}d\tau_1d\tau_2, \tag{4}$$

and

$$\frac{1}{(E_d-E_c)^2}\int\int\Psi_d^*\left(\frac{z_1}{r_1^3}+\frac{z_2}{r_2^3}\right)\Psi_{ci}d\tau_1d\tau_2. \tag{5}$$

Hence, the equality of expressions (2), (4), and (5) is a necessary condition for the correct wave functions.

Another set of necessary conditions for the correct wave functions and total absorption coefficient are the $\langle r^2\rangle_{\text{Av}}$ and $f$ sum rules[10]:

$$\frac{3}{2\pi}\frac{mc}{ha_0}\int_{\nu_0}^{\infty}\frac{\kappa_\nu}{\nu}d\nu=\int\int\Psi_d^*(r_1^2+r_2^2)\Psi_d d\tau_1d\tau_2, \tag{6}$$

and

$$\frac{mc}{\pi e^2}\int_{\nu_0}^{\infty}\kappa_\nu d\nu=2, \tag{7}$$

where $\nu_0$ is the frequency of the absorption limit. These sum rules have as their basis the fact that all the solutions of Eq. (3) form a complete set and the assumption that there is only one state in which both electrons are bound (the existence of only one bound state for $H^-$ has not been proved but is generally accepted[11]). They have been used by previous authors as a test of their calculated values for $\kappa_{\nu 0}$. This procedure does not appear to be strictly correct, however, since the exact $\Psi_d$ and $\Psi_{c0}$'s do not form a complete set by themselves. One must use the total absorption coefficient in (6) and (7) rather than the partial one which corresponds to a particular final state for the hydrogen atom.

For $\Psi_d$ and $\Psi_{ci}$ we construct functions of the form

$$\varphi_0(r_1)\varphi_0(r_2), \tag{8}$$

and

$$\frac{1}{\sqrt{2}}\{\varphi_0(r_1)\varphi_k(\mathbf{r}_2)+\varphi_0(r_2)\varphi_k(\mathbf{r}_1)\}, \tag{9}$$

where $\varphi_0$ and $\varphi_k$ are eigenfunctions of the equation

$$\{\nabla^2-2V(r)+2E\}\varphi=0. \tag{10}$$

Our model for the level structure of $H^-$ is thus a set of singly indexed states instead of the true doubly indexed set. The spherical potential $V(r)$ is chosen such that it will yield only one bound state having an energy equal in magnitude to the accepted electron affinity of the hydrogen atom. The $\varphi$'s will then be orthogonal and may be normalized such that $\int|\varphi_0|^2d\tau=1$, and $\varphi_k$ is made to become a free wave of unit amplitude at large distances from the nucleus. With these conditions on the $\varphi$'s the dipole length, velocity, and acceleration matrix elements become, respectively,

$$\sqrt{2}\int\varphi_0^*z\varphi_kd\tau,\quad -\frac{\sqrt{2}}{E_d-E_c}\int\varphi_0^*\frac{\partial\varphi_k}{\partial z}d\tau,$$

and

$$\frac{\sqrt{2}}{(E_d-E_c)^2}\int\varphi_0^*\frac{z}{r^3}\varphi_kd\tau,$$

which are identical because the $\varphi$'s are exact solutions of Eq. (10) and $E_d-E_c=E_0-E_k=h\nu$. The sum rule conditions, (6) and (7), will be satisfied by virtue of the $\varphi$'s forming a complete orthonormal set of functions.

The above requirements on $\varphi$ can be met by an infinite number of types of potential wells for $V$ (i.e., Square, Gaussian, Yukawa, etc.), and consequently our choice will have no claim to being unique. In other words, the conditions we have imposed on the wave functions are necessary but not sufficient. On the basis of physical reasonableness and mathematical simplicity, we chose the cut-off Coulomb potential,[12]

$$V(r)=\begin{cases}\dfrac{1}{r_0}-\dfrac{1}{r}; & r\leqslant r_0\\[2mm] 0; & r\geqslant r_0.\end{cases} \tag{11}$$

The fact that the potential vanishes more rapidly than $r^{-1}$ at large distances insures that it will have a finite number of bound states. Also it qualitatively resembles the Hartree field of an atomic core.[13] The parameter $r_0$ is adjusted to give the desired bound state energy level.

The resulting bound state function is

$$\varphi_0=\begin{cases}\dfrac{N_0}{2\sqrt{\pi}}e^{-t_0r}{}_1F_1\left(1-\dfrac{1}{t_0};2;2t_0r\right); & r\leqslant r_0\\[2mm] \dfrac{N_0}{2\sqrt{\pi}}A\dfrac{e^{-k_0r}}{r}; & r\geqslant r_0,\end{cases} \tag{12}$$

where $N_0$ is the radial normalization constant, $A$ is a matching constant, $t_0=[(2/r_0)+k_0^2]^{\frac{1}{2}}$, and $k_0^2=2|E_0|$. The continuum states may be expanded in terms of Legendre polynomials as

$$\varphi_k=\sum_{l=0}^{\infty}\frac{i^l(2l+1)}{kr}P_l(\cos\theta)\chi_l(r;k), \tag{13}$$

in which $k^2=2E_k$. The only partial wave which contributes to the dipole matrix element is the $p$ wave,

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[10] S. Chandrasekhar and M. K. Krogdahl, Astrophys. J. **98**, 205 (1943).

[11] T. Y. Wu, Phys. Rev. **89**, 629 (1953).

[12] This type of potential was first used to describe atomic fields by W. P. Allis and P. M. Morse, Z. Physik **70**, 567 (1931).

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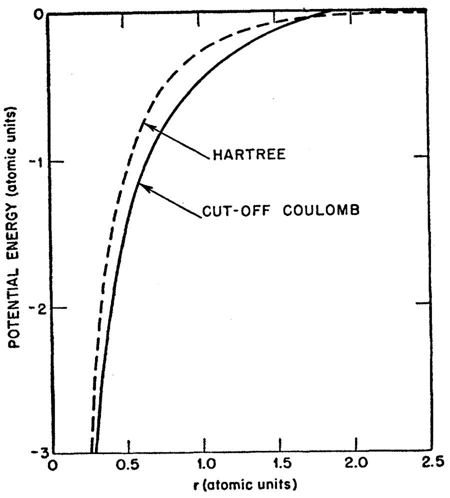

FIG. 1. Comparison of the cut-off Coulomb potential with the Hartree potential of a hydrogen atom.

which has the radial form

$$\chi_1=\begin{cases} N_1 r^2 e^{-tr}{}_1F_1\left(2-\dfrac{1}{t};4;2tr\right); & r\leqslant r_0\\[2ex] \dfrac{\sin(kr+\delta_1)}{kr}-\cos(kr+\delta_1); & r\geqslant r_0,\end{cases} \tag{14}$$

where $N_1$ is a matching constant, $t=[(2/r_0)-k^2]^{\frac{1}{2}}$, and $\delta_1$ is the phase shift. The formula for the total continuous absorption coefficient, in terms of these functions, becomes

$$\kappa_\nu=\frac{32\pi^2}{3}\alpha a_0^2\frac{k_0^2+k^2}{k}\left|\int_0^\infty \varphi_0\chi_1 r^2 dr\right|^2, \tag{15}$$

where $\alpha$ is the fine structure constant. The evaluation of the integral occurring above is performed numerically from 0 to $r_0$ and analytically from $r_0$ to $\infty$.

The best value for the electron affinity of the hydrogen atom is 0.747 ev.[6] Using this as the binding energy of a $1s$ level in Eq. (10) we obtain $r_0=1.88$ for the radius of our well. The resultant potential (11) is compared with the Hartree field, $-e^{-2r}(1+1/r)$, in Fig. 1. The greater depth of $V$ may be attributed to a polarization of the core by the "outer" electron.

The primary difference between the treatment for $\mathrm{Li}^-$ and $\mathrm{H}^-$ is the requirement that the two outer electrons in $\mathrm{Li}^-$ be in $2s$ orbitals. We regard the $1s$ shell of $\mathrm{Li}^-$ as essentially at the nucleus, making the procedure of the calculation identical to that for $\mathrm{H}^-$. Using the value of 0.384 ev for the electron affinity[14] of Li, we obtain $r_0=8.78$ (again assuming that there exists only one bound state). The results of the calculations are recorded in Table I and plotted on a wavelength scale in Figs. 2 and 3.

## III. VARIATIONAL TEST OF GROUND STATE FUNCTION

As an additional check on the correctness of our constructed ground state function for $\mathrm{H}^-$, we perform a Ritz variational calculation using a trial function having a similar form. We take for the trial function

$$\Psi_{dv}=\varphi_{0v}(r_1)\varphi_{0v}(r_2), \tag{16}$$

with

$$\varphi_{0v}=\begin{cases} \dfrac{N_v}{2\sqrt{\pi}}e^{-ar}; & r\leqslant r_{0v}\\[2ex] \dfrac{N_v}{2\sqrt{\pi}}A_v\dfrac{e^{-br}}{r}; & r\geqslant r_{0v}.\end{cases} \tag{17}$$

To secure continuity of $\varphi_{0v}$ and its derivative at $r_{0v}$, it is required that $r_{0v}=(a-b)^{-1}$ and $A_v=e^{-1}(a-b)^{-1}$, leaving only $a$ and $b$ as the variational parameters. The form of $\varphi_{0v}$ is identical to that of $\varphi_0$ for large $r$ where there is the greatest contribution to the dipole matrix element. For small $r$ the form of $\varphi_{0v}$ is sufficiently close to that of $\varphi_0$ because the confluent hypergeometric function is slowly varying compared to the exponential function.

The evaluation of the energy and normalization integrals requires separate intergrations over the three

TABLE I. Calculated continuous absorption coefficients of $\mathrm{H}^-$ and $\mathrm{Li}^-$.

| | $\mathrm{H}^-$ | | $\mathrm{Li}^-$ | |
|---|---|---|---|---|
| $k^2$ | $\lambda$(A) | $\kappa_\lambda$($10^{-17}$ cm$^2$) | $\lambda$(A) | $\kappa_\lambda$($10^{-17}$ cm$^2$) |
| 0 | 16533 | 0 | 32293 | 0 |
| 0.0025 | ... | ... | 29665 | 1.85 |
| 0.005 | 15158 | 0.69 | 27432 | 3.87 |
| 0.0075 | ... | ... | 25512 | 5.35 |
| 0.01 | 13994 | 1.54 | 23844 | 6.40 |
| 0.015 | 12996 | 2.26 | 21085 | 7.60 |
| 0.02 | 12131 | 2.83 | 18899 | 8.09 |
| 0.025 | ... | ... | 17123 | 8.18 |
| 0.03 | 10706 | 3.57 | 15653 | 8.08 |
| 0.035 | ... | ... | 14415 | 7.88 |
| 0.04 | 9581 | 3.95 | 13358 | 7.63 |
| 0.05 | 8669 | 4.09 | 11650 | 7.08 |
| 0.06 | 7916 | 4.10 | 10330 | 6.55 |
| 0.08 | 6744 | 3.91 | 8421 | 5.64 |
| 0.10 | 5875 | 3.62 | 7107 | 4.90 |
| 0.12 | 5204 | 3.31 | 6148 | 4.33 |
| 0.16 | 4236 | 2.76 | 4842 | 3.38 |
| 0.20 | 3572 | 2.31 | 3993 | 2.67 |
| 0.30 | 2566 | 1.58 | ... | ... |
| 0.40 | 2002 | 1.15 | ... | ... |
| 0.60 | 1391 | 0.69 | ... | ... |
| 1.00 | 864 | 0.33 | ... | ... |

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[14] For a review of the various evaluations of the electron affinity of Li, see B. L. Moiseiwitsch, Proc. Phys. Soc. (London) **A67**, 25 (1954). Using the latest spectroscopic data [C. E. Moore, *Atomic Energy Levels*, National Bureau of Standards, Circular No. 467 (U. S. Government Printing Office, Washington, D. C., 1949)] in the quadratic extrapolation from isoelectronic systems, 0.733 ev and 0.377 ev are obtained for the affinities of H and Li, respectively. If we accept Henrich's value of 0.747 ev as the true affinity for H and assume that the extrapolation underestimates the true value by the same fractional amount in both cases, we obtain 0.384 ev for the electron affinity of Li.

regions of $r_1r_2$ space (since function is symmetric): $r_1$ and $r_2 \leqslant r_{0v}$, $r_1 \leqslant r_{0v}$ and $r_2 \geqslant r_{0v}$, $r_1$ and $r_2 \geqslant r_{0v}$. The integrals which arise are straightforward and easily carried through. The energy minimum is found numerically to be $-0.4850$, with the corresponding parameters $a=0.808$ and $b=0.259$. Of course, this energy is considerably higher than that obtained with trial functions containing many more parameters. In fact, this energy is too high to permit a bound state of $H^-$ to exist. However, what is important to establish the validity of our calculated absorption coefficient is the comparison of this variational function at minimum energy with our constructed ground state function. This comparison, given in Table II, is reasonably favorable over the region of $r$ which contributes most to the dipole matrix element. It is also of interest to note that $r_{0v}=1.82$ as compared with $r_0=1.88$.

The principal difference between our present trial function and those previously employed is its asymptotic form corresponding to complete shielding, $r^{-1}e^{-br}$, rather than that of a screened Coulomb field, $e^{-br}$. This type of asymptotic behavior is more reasonable for the description of an electron in $H^-$ than it would be in He because the electron-electron interaction is relatively more important in the former case. It is this fact which may cause the energy of $H^-$ to converge less rapidly than that of He as the trial function is given more parameters.[7] It appears that the best ground state wave function for $H^-$ for the calculation of both minimum energy and the absorption coefficient would be a Hylleraas-type function modified so that it will asymptotically assume the completely shielded form.

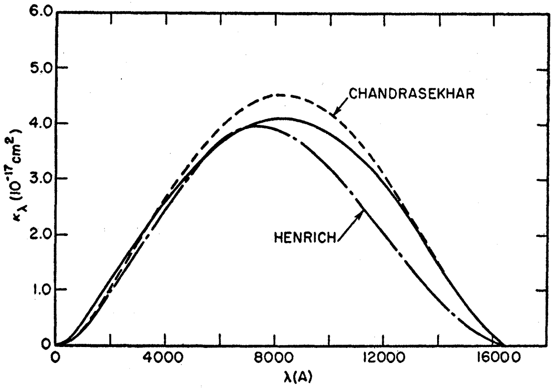

FIG. 2. Calculated continuous absorption coefficient of $H^-$ (solid line). Henrich's calculation[6] is with an 11 parameter ground state function and the dipole length matrix element. Chandrasekhar[9] makes use of the same 11 parameter function and the dipole velocity matrix element.

## IV. CONCLUDING REMARKS

The comparison (Fig. 2) of our present result for $H^-$ with the latest previous calculations (for $\kappa_{\nu 0}$) shows relatively close agreement. The experimental electron photodetachment currents[1] were found to be consistent with Chandrasekhar's calculation, but they would be equally consistent with the present result to within the experimental uncertainty.[15] The fact that our absorption coefficient exceeds the previously calculated curves[6,9] at small wavelengths is perhaps due to the inclusion in our model of the average effect of transitions to excited states of the hydrogen atom while previous workers consider only the transition to the ground state. The absorption coefficient of $Li^-$ has not been previously investigated, either experimentally or theoretically.

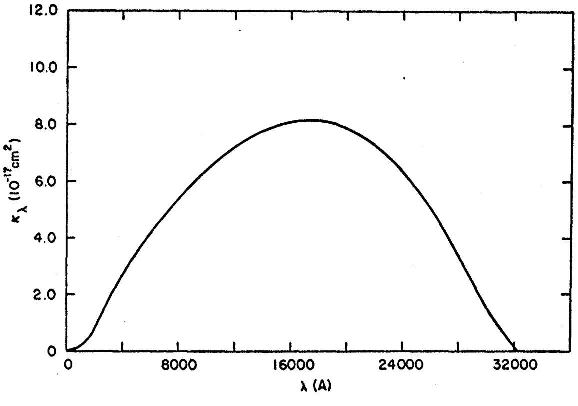

FIG. 3. Calculated continuous absorption coefficient of $Li^-$.

A natural question which arises is to what extent the methods employed here are applicable to other transitions. The case of negative ions is particularly favorable since the existence of only one bound state (or very few) makes the choice of $V(r)$ relatively simple. In a neutral atom or positive ion, the presence of an infinite number of bound states would make the selection of a suitable one-electron potential very difficult. For a given discrete transition, one could take a reasonably shaped potential containing several adjustable parameters and fix them so that two of the eigenvalues coincide with the exact energies of the initial and final states. This would

TABLE II. Comparison of constructed and variational one-electron ground state wave functions for $H^-$.

| $r$ | $\varphi_0$ | $\varphi_{0v}$ |
|---|---|---|
| 0 | 0.428 | 0.363 |
| 0.5 | 0.266 | 0.242 |
| 1.0 | 0.171 | 0.162 |
| 1.5 | 0.108 | 0.108 |
| 2.0 | 0.0689 | 0.0724 |
| 3.0 | 0.0364 | 0.0372 |
| 4.0 | 0.0216 | 0.0216 |
| 6.0 | 0.00903 | 0.00856 |
| 8.0 | 0.00425 | 0.00383 |
| 10.0 | 0.00210 | 0.00182 |
| 12.0 | 0.00109 | 0.000906 |
| 14.0 | 0.000584 | 0.000462 |
| 16.0 | 0.000321 | 0.000240 |
| 20.0 | 0.000100 | 0.0000685 |

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[15] L. M. Branscomb and S. J. Smith (private communication).

insure the equivalence of the three forms for the dipole matrix element between these particular states. A different transition in the same atomic system would in general require the readjustment of the potential parameters. The degree to which a given choice of parameters yields the correct energy levels for all of the important transitions may be used as a criterion for the reliability of the results.

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# Electronic Theory of Local Order

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The application of the perturbed free-electron approximation to a binary metallic solid solution leads to an expression for the energy which includes a term dependent on the local order. As a consequence of this term, and in the absence of other effects, short-range order is predicted for solid solutions with an electron/atom ratio of about one, and clustering for solid solutions with an electron/atom ratio between two and three. The sign and order of magnitude of the effect observed in several alloys where this approach may be appropriate is consistent with that calculated by this method.

## INTRODUCTION

FOR most purposes, metallic solid solutions are usually regarded as being derived from a perfect monatomic lattice by the random replacement of solvent atoms by solute atoms. Although the existence of nonrandom solutions has long been realized, the importance of the deviations from randomness, "local order," has only recently been recognized. In current theories of solid-solution hardening, however, local order plays an important part.[1] The kinetics of precipitation may also be expected to depend to a considerable extent on the local structure of the parent solid solution. Direct experimental information from x-ray or neutron diffraction about the amount and kind of local order in an alloy is difficult to obtain, and exists for relatively few systems, while inferences based on electrical, magnetic, or thermodynamic measurements, although widely used, are unfortunately quite unreliable. It seems worth while, therefore, to have a simple approximate theory, somewhat analogous to the Jones theory of alloy phases, and with similar limitations, which may make it possible in some cases to estimate the kind and amount of local order likely to be present.

## DEFINITION OF LOCAL ORDER

Before proceeding to the details of the calculation, it may be well to discuss the definition of local order. Historically, the term "short-range order" developed out of a study of superlattices, and is generally associated with that type of deviation from randomness in which the average number of unlike nearest neighbors is greater than the random number. The opposite situation, in which the average number of unlike nearest neighbors is less than the random number, sometimes known as "clustering," has been observed more recently.[2,3] Somewhat arbitrarily, both of these effects and the generalization to other than nearest neighbors will be referred to herein as "local order." For the quantitative description of local order, various parameters have been suggested. Perhaps the best known and most convenient is that of Cowley.[4] His definition (with a slight change in notation) is

$$\alpha_{\mathrm{r}} = 1 - (p_{\mathrm{r}}/m_A), \tag{1}$$

where $p_{\mathrm{r}}$ is the probability of finding an $A$ atom displaced by a vector $\mathbf{r}$ from a $B$ atom, and $m_A$ is the fraction of $A$ atoms. For a random solution, all $\alpha$'s are zero; for short-range order, the average value of the alphas for the $\mathbf{r}$ vectors connecting nearest neighbors is negative; for clustering, it is positive. If the roles of $A$ and $B$ atoms are interchanged in the definition, the value of $\alpha$ is unaffected. This symmetry of $\alpha$ may be shown by the following alternative method of definition. We will describe the local structure of the lattice in terms of the correlation of atom positions, averaged over the lattice, rather than in terms of the probable neighbors of one atom, and show the two definitions to be equivalent. We may specify the makeup of a

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[1] J. C. Fisher, Acta Metallurgica **2**, 9 (1954).

[2] Walker, Blin, and Guinier, Compt. rend. **235**, 254 (1952).

[3] P. S. Rudman and B. L. Averbach, Acta Metallurgica **2**, 576 (1954).

[4] J. M. Cowley, Phys. Rev. **77**, 669 (1950).