TABLE I. Na_2 A-state lifetimes.

Vibrational level	Lifetimes (nsec)
$v = 1$	12.2 ± 0.3
$v = 2$	12.3 ± 0.4
$v = 6$	12.3 ± 0.3
$v = 7$	12.8 ± 0.5
$v = 21$	12.9 ± 0.3
$v = 22$	12.6 ± 0.2
$v = 24$	13.0 ± 0.2
$v = 25$	12.8 ± 0.2

molecular constants for the ground state from Demtröder, McClintock, and Zare,[3] and for the excited A state from Herzberg.[4] Identification of the vibrational terms was confirmed by displaying the fluorescence spectrum for about 30 bands.

Table I shows results obtained for lifetimes of A-state levels lying in the range $v' = 1$ to $v' = 25$. The data was fit to an exponential by a least squares routine. Our measurement and fitting procedures were tested by observing the decay fluorescence of the $3p$ state of atomic sodium. Data for each v' level was acquired in at least two independent runs. We estimate that non-statistical errors are approximately 0.1 nsec. The final error shown is based on the standard deviation of single runs and our best estimate of uncertainty due to systematic errors.

The values obtained—all in the 12–13 nsec regime—are in general agreement with recent theoretical predictions.[5] To within our errors no significant trend is observed as a function of v'.[6]

A study of Na_2 lifetimes by argon ion laser excitation has yielded lifetimes for two levels which were tentatively assigned to the A state, and which are consistent with our results.[7]

This spectroscopic technique, employing pulsed tunable dye lasers and molecular beams, provides a particularly simple and straightforward way to extract lifetimes of individual molecular states. With a spectrally narrower laser individual (v', J') levels can be populated and an even more detailed probe of the molecular potentials can be obtained.

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Determination of Madelung constants for infinite and semi-infinite lattices by direct summation

J. V. Calara and J. D. Miller

Department of Mining, Metallurgical, and Fuels Engineering, University of Utah, Salt Lake City, Utah 84112

Lattice sums for the electrostatic interactions in ionic crystals, first evaluated by Madelung,[1] are now known to high degrees of accuracy.[2] The problem of conditional convergence has been solved either by manipulations of a mathematical model of the lattice,[1,3–5] or by directly summing over neutral groups of the lattice as was done by Evjen[6] and Frank.[7] Although the first method has been modified and extended to encompass semi-infinite lattices,[8,9] there are no corresponding works on direct summation techniques. Dahl[10] has corrected the Evjen method to expand its range to more complex crystals but did not indicate its applicability to bounded lattices. This communication describes a novel direct summation approach broad enough to handle any infinite or semi-infinite lattice that can be decomposed into finite, neutral, linear charge arrays. The technique is unique in that it is the only direct summation method demonstrated capable of calculating surface Madelung constants.

In common with other direct summation procedures, the summation is made absolutely convergent by grouping the charges into neutral, linear repeating units, the potential of which decays rapidly with respect to the distance r from the point at which the potential is being evaluated. Since the summation is three dimensional, the potential due to a repeat unit must at least decay with r^{-4} in order to assure convergence. This condition is satisfied if the charge array (the repeat unit) has vanishing electric moments up to and including the quadrupole, or higher. For example, Fig. 1 illustrates the repeat units selected for NaCl, CsCl, and CaF_2, all belonging to the cubic system but with different Bravais lattices.

The repeat units may be arranged in any growth geometry as long as they are appropriately overlapped to
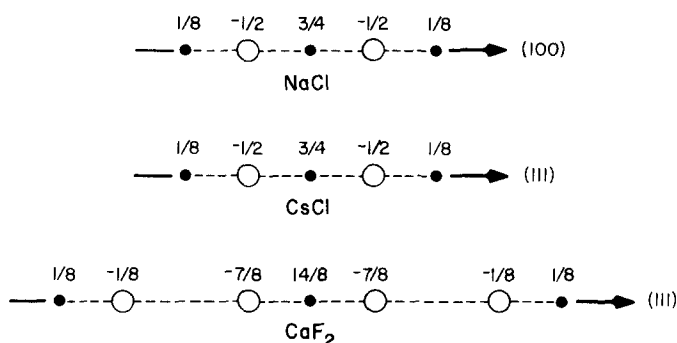
FIG. 1. Repeat units for three different cubic lattices. Arrows indicate the units' crystallographic orientation.

TABLE I. Madelung constants for infinite and semi-infinite lattices. All values referred to cationic site and cubic or pseudocubic unit cell's edge.

Crystal		Madelung constant		
	Direct sums	Calculated	Literature	Reference
NaCl, bulk	$V^+ = 3.503644$ $V^- = 3.486580$	3.495122	3.495129	2
NaCl, surface	$V_s^+ = 3.3278$	3.3288	3.34	12
CsCl, bulk	$V^+ =$ $V^- =$	2.03515	2.03536	2
CaF$_2$, bulk	$V^+ = 15.140794$ $V^- = 4.049869$	11.63659	11.636575	2
CaF$_2$, (111) surface	$V_s^+ = 13.817803$	12.04467	none	

reproduce the crystal lattice upon summation. If we evaluate the potential sum around an interior reference cation, we obtain the direct sum V^+. This is *not* the Madelung sum for that ion, but rather the Madelung sum plus a constant ξ which is traceable to the surface structure whenever the summation is stopped. The choice of different linear repeat units for the same lattice leads to different values of this additive constant because of the differences in the surface specifications of the mathematical crystal.[11] The surface contribution ξ is dipolar in nature and can be eliminated by considering the fact that it is opposite in sign for oppositely charged reference ions. Thus for symmetrical ionic solids such as NaCl and CsCl, if V^+ and V^- are the direct sums about an interior cation and an anion, respectively, and A is the Madelung constant, we have

$$V^+ = A + \xi , \tag{1}$$

$$V^- = A - \xi . \tag{2}$$

Eliminating the surface contribution, the Madelung constant is found to be:

$$A = \tfrac{1}{2}(V^+ + V^-) . \tag{3}$$

In general, for a binary ionic lattice $X_m Y_n$ where ions of the same charge have identical environments,

$$A = \tfrac{1}{2}[V^+ + (n/m) V^-] \tag{4}$$

for the cation, and

$$A = \tfrac{1}{2}[(m/n) V^+ + V^-] , \tag{5}$$

for the anion.

With regard to a semi-infinite lattice, the dipolar

surface contribution ξ is only half of that for an infinite lattice. The application of this direct summation technique to surfaces is without difficulty. For example, in the case of NaCl, if a sodium ion in the (100) cleavage surface is considered as the reference point, the direct sum, V_s^+, can be computed and the surface Madelung constant would be

$$A_s = V_s^+ + \tfrac{1}{2} \xi , \tag{6}$$

where ξ is obtained from Eqs. (1) and (2). The direct sum may include contributions from repeat units that may have been partly truncated by the cleavage surface. Therefore care must be exercised in orienting the repeat units such that the hemicrystal remains electrically neutral after cleavage is effected. This is particularly critical for the polar cleavage surface of CaF$_2$. Table I summarizes results obtained for the NaCl, CsCl, and CaF$_2$ lattices. All values are referred to the cubic cell's edge.

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The calculation of nuclear spin coupling constants from LCAO–SCF–$X\alpha$ wavefunctions

Hiroyuki Fukui

Kitami Institute of Technology, 165 Koencho, Kitami 090, Japan
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The recently developed Hartree–Fock–Slater (or SCF–$X\alpha$) method for molecules[1-3] has been successfully employed to predict ionization energies of a variety of systems.[4-6] Until now, however, calculations for physical properties other than ionization energies have not been reported. It has not been known how