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Modified Broyden's method for accelerating convergence in self-consistent calculations

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A modification to Broyden's method for obtaining stable and computationally efficient convergence in self-consistent calculations is developed and discussed. The method incorporates the advantages of two schemes proposed by Srivastava and by Vanderbilt and Louie without any increase in complexity. Its improvement over their methods is discussed. The present method is compared with two other widely used convergence methods, simple mixing and Anderson's method, for the case of the disordered binary alloy $\text{Ni}_{0.35}\text{Fe}_{0.65}$ on the verge of a magnetic instability and is shown to be much improved in stability and rate of convergence.

I. INTRODUCTION

The self-consistent solution of coupled, nonlinear equations is a treasured topic in numerical analysis. We discuss an improved algorithm, primarily in the context of electronic-structure calculations, for obtaining stable and computationally efficient convergence for iterative solutions.

In electronic-structure calculations, it is necessary to determine the charge density by solving the Kohn-Sham equations self-consistently. For density-functional-based calculations, the charge density $n(\mathbf{r})$ is given in terms of the one-electron wave functions, which depend nonlinearly on $n(\mathbf{r})$ through the effective one-electron potential $V(\mathbf{r})$. The prescription for obtaining $V(\mathbf{r})$ from $n(\mathbf{r})$ is given within density-functional theory via Poisson's equation plus a many-body contribution, e.g., in the local approximation.¹ The self-consistency condition for this type of calculation can be written as $F(n) = n_{\text{out}}(n) - n = 0$, where n is the input density. Therefore, in essence, one is just solving a system of simultaneous nonlinear equations $F(n) = 0$. Note, it is equally valid to consider convergence of $V(\mathbf{r})$, since both the charge and the potential convergence are equivalent when they are treated symmetrically, except that the total energy need not converge as rapidly when the potential convergence is used.

In an iterative procedure, convergence can be defined as continuously minimizing the "distance" between the input and output charge densities. When this distance is zero, i.e., input and output densities are equal, we say the system has converged to the fixed-point solution. The simplest definition of distance between the input and output densities, using Dirac notation, is

$$D[n_{\text{out}}, n] \equiv (\langle n_{\text{out}} - n | n_{\text{out}} - n \rangle)^{1/2} \\ = \langle F(n) | F(n) \rangle^{1/2}, \quad (1)$$

i.e., the norm of the vector F .

Typically, instabilities occur while solving systems of nonlinear equations by straight iteration. In the electronic-structure case, this feature is exhibited by the development of charge oscillations during the iterative cycle, which if left unchecked would cause divergence of the algorithm. To obtain convergence, $D \rightarrow 0$, various methods are used to damp these oscillation during the iterative process.

In the next section, we discuss three methods used to damp these oscillations and obtain convergence, each successively more sophisticated. This brief survey is useful for the sake of comparisons to be made with the modified method to be presented in this paper. In Sec. III, the algorithm which is based on Newton-Raphson techniques is developed. A discussion of the modification will follow in Sec. IV. And, finally, in the last section, results and a comparison with the other methods will be presented.

II. BRIEF SURVEY OF CONVERGENCE ALGORITHMS

A. Simple mixing

The most simple-minded method to damp charge oscillations during the iterative process is to use a linear combination of input and output densities as the input charge density to the next iteration, i.e.,

$$|n^{(m+1)}\rangle = (1 - \alpha)|n^{(m)}\rangle + \alpha|n_{\text{out}}^{(m)}\rangle = |n^{(m)}\rangle + \alpha|F^{(m)}\rangle, \quad (2)$$

where the superscript m denotes the particular iteration. In most cases, by a suitable choice of $\alpha \in [0, 1]$, convergence can usually be achieved. However, there are many instances where this is not true, or convergence proceeds very slowly with an excessive number of iterations, such as can be the case with the onset of magnetism, for example, where $\alpha \leq 0.01$ is not unusual. Realistically, a better iterative method is necessary. A formal study of simple mixing in electronic-structure calculations near convergence was performed by Dederichs and Zeller² which gave constraints on α for various types of calculations.

B. Anderson's mixing

Anderson's method,³ as proposed by Hamann⁴ for electronic-structure calculations, is an extension of the simple mixing scheme of Eq. (2). The relationship of the mixed input (output) density is assumed linear in the true input (output) density, i.e.,

$$|\bar{n}_{\text{in(out)}}\rangle = (1 - \beta)|n_{\text{in(out)}}^{(m)}\rangle + \beta|n_{\text{in(out)}}^{(m-1)}\rangle. \quad (3)$$

The aim is to obtain the "best" β value for the current iteration with which to minimize the distance between these two "average" densities. By setting $\partial D[|\bar{n}_{\text{in}}, \bar{n}_{\text{out}}\rangle] / \partial \beta = 0$, we obtain for β

$$\beta = \frac{\langle F^{(m)} | F^{(m)} - F^{(m-1)} \rangle}{D^2[F^{(m)}, F^{(m-1)}]}. \quad (4)$$

Finally, to obtain the new guess for the next iteration, we simply mix the average input and output densities, as in Eq. (2), where the mixing parameter α is again chosen empirically,

$$|n^{(m+1)}\rangle = (1 - \alpha)|\bar{n}_{\text{in}}^{(m)}\rangle + \alpha|\bar{n}_{\text{out}}^{(m)}\rangle. \quad (5)$$

This is necessary so that the new iterate does not become mired in a subspace spanned by the old iterates only, and D remains at some nonzero value. This method was independently proposed by Pulay,⁵ who used it for molecular calculations.

[For the case of spin-polarized (magnetic) calculations, there are two possible vectors that can be constructed in order to use Anderson's method as described in Eqs. (3)–(5). While above the vector n is the total charge density, this vector can be replaced either by a vector composed of the majority and the minority charge densities or by a vector composed of the total charge and magnetization densities for the spin-polarized calculations. If one writes down the distance D for these two definitions of the vector, it will be evident that there are different cross terms which appear, and, therefore, they are not equivalent. In fact, the former definition is always more stable than the latter. The latter definition of the vector is sometimes more useful, however, when the vector is far from convergence. Please keep in mind that in the results to be given for the case of a magnetic instability Anderson's method will refer to the method which uses the first, more stable, definition.]

[A final point about the spin-polarized case. When performing the simple mix as required by Eq. (2) or Eq. (5), the magnetization density may be mixed with a

different mixing parameter than the charge density, regardless of the definition of the vector. That this is useful can be seen as follows. Since the magnetization density is less susceptible to long-wavelength charge fluctuation than is the total charge density,⁶ it may always be mixed with a larger mixing parameter, and, therefore, it may converge more rapidly.]

It should be noted here that the values of β can vary dramatically, and in some cases become negative. This is quite different than what is a typical value of α in Eq. (2), $\alpha \in [0, 1]$. Moreover, it is usually very beneficial for β to take on negative values, as long as $\partial^2 D / \partial^2 \beta > 0$.

Our experience has been that using this method but including a third-iteration density is more beneficial and less unstable. The counterpart to Eq. (4) in this case is the solution of a matrix equation for α . This method is much improved over Eq. (2); it can obtain convergence in some cases where Eq. (2) is useless and Eqs. (3)–(5) are of questionable benefit. One might be tempted, therefore, to continue this process, including more input-output densities, to speed up convergence further. However, it should be fairly obvious that as the iterative process approaches convergence, linear dependencies develop and the matrix solution of β diverges, and no solution is possible. From experience, we find that keeping three or four iterations of input-output densities is best, typically three is optimal.

A final point, as in Eq. (2), the Anderson method of mixing only updates the density at each r point in a one-to-one correspondence. That is, no information from other r points is allowed to affect a particular r point during the mix. This is the major shortcoming of this method. If, for example, there is a large amount of charge transfer, an r -dependent mixing scheme should greatly improve convergence. In this case, a more sophisticated scheme is necessary.

C. Broyden's method

Of several iterative methods available to solve systems of nonlinear equations, the most sophisticated procedure for constructing a new input quantity is Broyden's quasi-Newton-Raphson (Jacobian update) method.⁷ This technique has been used in electronic calculations on a variety of systems, always with a significant reduction in the number of iterations necessary for convergence as compared to the simple mixing procedure. However, a shortcoming of the method is the prohibitive storage required in keeping the updated $N \times N$ Jacobian, where N is the length of the vector (in this case, the number of r points) to be updated, and the necessity of large matrix multiplications. N can be a large number, on the order of 10 000 or more, depending on the problem.

Recently, Srivastava⁸ derived Broyden's second (inverse Jacobian update) method in a manner which avoids the $N \times N$ matrix storage problem as well as $N \times N$ matrix multiplications. Only storage of m vectors of length N are required, where m is the number of iterations. This method is a computationally efficient scheme and has been used successfully for both bulk and surface calculations. There is, however, a drawback to this method. In-

formation from the current iteration is allowed to update the inverse Jacobian, but is also allowed to override information from previous iterations.

In this procedure, one approximates $F(n)$ at the m th iteration by

$$|F(n)\rangle \approx |F(n^{(m)})\rangle + J^{(m)}(|n\rangle - |n^{(m)}\rangle). \quad (6)$$

(One should keep in mind that for the present discussion n is the density; however, n may represent any vector variable which is to be iterated.) For $F^{(m+1)}$ to equal zero, the right-hand side must vanish. This leads to an update equation for the vector $n^{(m+1)}$, i.e.,

$$|n^{(m+1)}\rangle = |n^{(m)}\rangle + G^{(m)}|F^{(m)}\rangle = |n^{(m)}\rangle + |\eta^{(m)}\rangle, \quad (7)$$

where $G^{(m)} = -(J^{(m)})^{-1}$. However, it is most often the case that $|F^{(m+1)}\rangle$ is not zero, and we may recast Eq. (6) as

$$|\Delta n^{(m)}\rangle + G^{(m)}|\Delta F^{(m)}\rangle = 0, \quad (8)$$

where it is both convenient and an advantage numerically to work with scaled vectors defined as follows:

$$|\Delta n^{(m)}\rangle = \frac{|n^{(m+1)}\rangle - |n^{(m)}\rangle}{\left| |F^{(m+1)}\rangle - |F^{(m)}\rangle \right|}, \quad (9)$$

and $|\Delta F^{(m)}\rangle$ is defined by replacing n with F . Note, using this definition, $\langle \Delta F^{(m)} | \Delta F^{(m)} \rangle \equiv 1$.

In Broyden's second method, $G^{(m)}$ fails generally to satisfy Eq. (8). So, $G^{(m+1)}$ is updated by requiring $\|G^{(m+1)} - G^{(m)}\|$ to be minimized subject the constraint of satisfying Eq. (8). This procedure results in the following update of G :

$$G^{(m+1)} = G^{(m)} - (|\Delta n^{(m)}\rangle + G^{(m)}|\Delta F^{(m)}\rangle)\langle \Delta F^{(m)}| \quad (10)$$

It is noted readily that $G^{(m+1)} - G^{(m)}$ is a matrix of rank 1, hence this is known as a rank-1 updating procedure. As a consequence of this, G of Eq. (10) does not satisfy Eq. (8) for all previous iterations ($n < m$), as it should. Thus, information from previous iterations has been overridden arbitrarily by information from the current iteration.

III. MODIFICATION OF BROYDEN'S METHOD

Vanderbilt and Louie⁹ (VL) have suggested and used successfully a modified version of Broyden's method in which they incorporate information from all previous iterations during the updating procedure. They noted an improved convergence over the standard Broyden's method, as well as convergence of the Jacobian to its true value; however, the storing and the multiplications of $N \times N$ matrices remain as a shortcoming of their method.

We now show that it is possible to use the modifications of Vanderbilt and Louie within Broyden's second method and obtain a similar computational scheme to that of Srivastava. Thereby, the advantages of both algorithms are obtained.

As VL argued, an update which disregards previous information results in too severe an alteration of $G^{(m+1)}$, and, therefore, $G^{(m+1)}$ should be forced to satisfy Eq. (8) as best as possible. Thus, following their suggestion for

the update of the Jacobian, we determine the update of the inverse Jacobian, $G^{(m+1)}$, by a least-squares minimization of an "error function," where a weight w_n is associated with each previous iteration and a weight w_0 assigned to the error in the inverse Jacobian. Thus, with the error function defined as

$$E = w_0^2 \|G^{(m+1)} - G^{(m)}\|^2 + \sum_{n=1}^m w_n^2 |\Delta n^{(n)} + G^{(m+1)}|\Delta F^{(n)}|^2,$$

we set $\partial E / \partial G_{ij}^{(m+1)} = 0$, which gives

$$G^{(m+1)} = A^{(m+1)}(B^{(m+1)})^{-1}, \quad (11)$$

where

$$A^{(m+1)} = w_0^2 G^{(m)} - \sum_{n=1}^m w_n^2 |\Delta n^{(n)}\rangle \langle \Delta F^{(n)}| \quad (11a)$$

and

$$B^{(m+1)} = w_0^2 I + \sum_{n=1}^m w_n^2 |\Delta F^{(n)}\rangle \langle \Delta F^{(n)}|. \quad (11b)$$

At this point, we choose a different approach than VL. By expanding $(B^{(m+1)})^{-1}$ to infinite order in terms of the vector ΔF , then resumming, it follows that no explicit matrix inversion ever needs to be performed and

$$(B^{(m+1)})^{-1} = (w_0)^{-2} \left[I - \sum_{k,n=1}^m w_n w_k \beta_{kn} |\Delta F^{(n)}\rangle \langle \Delta F^{(k)}| \right] \quad (12)$$

with

$$\beta_{kn} = (w_0^2 I + a)^{-1}_{kn}, \quad a_{ij} = w_i w_j |\Delta F^{(j)}\rangle \langle \Delta F^{(i)}|, \quad (13a)$$

see the Appendix. Note that the matrices in Eq. (13a) are small $m \times m$, not large $N \times N$, matrices. Then, using this result in Eq. (11), it follows that

$$G^{(m+1)} = G^{(m)} - \sum_{k,n=1}^m \beta_{kn} (G^{(m)}|\Delta F^{(n)}\rangle + |\Delta n^{(n)}\rangle)\langle \Delta F^{(k)}|. \quad (13b)$$

It is useful to put $G^{(m+1)}$ in terms of $G^{(1)}$. This is easily accomplished by induction, and we obtain

$$G^{(m+1)} = G^{(1)} - \sum_{k=1}^m |Z_k^{(m)}\rangle \langle \Delta F^{(k)}|,$$

where

$$|Z_k^{(m)}\rangle = \sum_{n=1}^m \beta_{kn} |u^{(n)}\rangle + w_0^2 \sum_{n=1}^{m-1} \beta_{kn} |Z_n^{(m-1)}\rangle$$

and

$$|u^{(n)}\rangle = G^{(1)}|\Delta F^{(n)}\rangle + |\Delta n^{(n)}\rangle. \quad (13b)$$

This equation for $G^{(m+1)}$ is no more complicated than the similar one obtained by Srivastava and just as easy to implement. However, for w_0 small, we obtain a very simple equation for the update of G , i.e.,

$$G^{(m+1)} = G^{(1)} - \sum_{k,n=1}^m \beta_{kn} |u^{(n)}\rangle \langle \Delta F^{(k)}| + O(w_0^2). \quad (14)$$

In this limit, we are only minimizing $\|G^{(m+1)} - G^{(1)}\|$. Moreover, if we also take the limit $w_n \ll 1$ for $n < m$ and the weights are independent of the iteration number, we obtain the standard Broyden's second method. In this limit, the update to $|n^{(m)}\rangle$ now follows directly from Eq. (7) and is relatively simple, i.e.,

$$|n^{(m+1)}\rangle = |n^{(m)}\rangle + G^{(1)}|F^{(m)}\rangle - \sum_{n=1}^{m-1} w_n \gamma_{mn} |u^{(n)}\rangle, \quad (15a)$$

where

$$\gamma_{ml} = \sum_{k=1}^{m-1} c_k^m \beta_{kl} \quad \text{and} \quad c_k^m = w_k \langle \Delta F^{(k)} | F^{(m)} \rangle. \quad (15b)$$

Equations (13) and (15) constitute all the information that is required for the updating of the vector. One must save only the current vectors $|n\rangle$ and $|F\rangle$, the vectors $|u\rangle$ and $\langle \Delta F|$ from all previous iterations, and, for efficiency, the matrix a_{ij} . This results in a storage of one $m \times m$ matrix and of mN vectors, as in Srivastava's algorithm. If the weights are chosen to be iteration dependent, as will be discussed, then m weights must also be stored.

It only remains to choose an appropriate $G^{(1)}$. Although G can be related to the dielectric kernel in the case of electronic-structure calculations, it is more straightforward to choose it as a diagonal constant matrix, i.e., $G^{(1)} = \alpha I$. In this case, we see that the first two terms of Eq. (15) just give us the linear mixing of Eq. (1), and the last term is the correction to this. According to Powell,¹⁰ the appropriate choice of α should be such that $\langle F^{(2)} | F^{(2)} \rangle < \langle F^{(1)} | F^{(1)} \rangle$; however, experience has shown that α may be chosen rather large compared to that in the simple mixing and Anderson mixing schemes. Other choices for the functional form of $G^{(1)}$ may be envisaged, however, the choice must lead to a charge-conserving guess for the new vector.

IV. DISCUSSION

Several comments are necessary before proceeding with an example. First, from Eq. (15), it follows that only m vectors of length N need be kept to renew the guess of vector. No storage or multiplications of $N \times N$ matrices are necessary. Second, as VL noted, the weights associated with each iteration add considerable flexibility to the convergence process. For example, more recent iterations may be given greater influence than earlier iterations, where, say, Brillouin zone integrals or basis sets are less than optimal. If the vector is composed of the charge density, one physically appropriate choice of the weights would be $w_m = \langle F^{(m)} | F^{(m)} \rangle^{-1/2}$, i.e., the inverse of the rms difference of the charge density. So, as convergence is approached, the larger the weights associated with that iteration become. It is found in practice that the weights should not be less than 1.

Third, when the initial density is very far from convergence, one might expect the performance of any

Broyden's method to suffer since they are linear methods. In order not to sustain a memory effect and obtain faster convergence, it is sometimes beneficial to restart the Broyden's method after a few iterations. In fact, it may be even beneficial to redefine the vector when one restarts the method. This is illustrated in the example to be discussed.

Fourth, by choosing the initial guess of the vector $|n\rangle$ to be charge conserving, it is easily shown from Eq. (15) that the algorithm remains charge conserving (see comment, Ref. 11). Fifth, the vector to be updated need not be simply the charge density or the potential. The vector may be composed of several elements that are interdependent, although not necessarily directly so. For instance, the total individual charge densities and the individual magnetization densities may be put contiguously together to compose the vector. Or, as suggested by Bendt and Zunger,¹² the Coulomb and exchange-correlation potentials may be mixed separately in order to obtain faster convergence.

Sixth, of whatever the vector is composed, it may be important that the elements of the vector be chosen somewhat judiciously, as far as relative magnitudes, for example. That this may be necessary can be seen as follows. Broyden's methods are based on minimizing the norm of the difference of two successive (inverse) Jacobians which were generated from the vectors $|n\rangle$. No information of the second derivatives (the Hessian) is used; therefore, the curvature of the solution space is not known *a priori*, and, as in all Newton-Raphson techniques, a "good" guess of the initial vector is important. Suppose the vector has two sets of elements, say, $|n\rangle = |n_1, n_2\rangle$. With $\langle n_2 | n_2 \rangle \gg \langle n_1 | n_1 \rangle$, it is possible that the elements of n_2 will be considered preferentially in the update of the (inverse) Jacobian, even though the relative importance of the elements n_1 may be greater. This would be exhibited by convergence in the elements n_1 and slow convergence, or divergence, in the elements n_2 .

In the simple model proposed by Vanderbilt and Louie, it is possible to investigate what effect a poor choice of the initial elements in the vector has. For some elements much larger than the others, one obtains convergence (divergence) in the elements "near" ("far") from their correct solution. There can be borderline choices of the magnitudes of the elements in which it is necessary to make a prudent choice in the initial (inverse) Jacobian, i.e., α . This results in convergence of the all elements, although at a cost of increased number of iterations.

A more subtle example of this has been experienced in FLAPW (full-potential, linear augmented-plane-wave) calculations using Srivastava's algorithm.¹³ In the FLAPW method, the vector was chosen to be composed of many elements, including total charge densities within a sphere about the site (TCD's) and a set of coefficients which describe the interstitial charge densities (ICD's). The elements of these two quantities are coupled in a very nonlinear fashion. Each of the ICD's is actually a bare Fourier coefficient scaled by the unit-cell volume and can be 2-3 orders of magnitude larger than the TCD's. In various cases, although the bare Fourier

coefficients were changing only slightly, the changes of the ICD's relative to that of the TCD's were large. The TCD elements converged, but the ICD elements continued to have crosstalk among one another and, thus, were not converging. This is a case where some elements of the vector, the ICD's, were chosen slightly outside the solution space and were solely responsible for the lack of convergence of the charge density within the unit cell, which is described by both the TCD's and the ICD's. In surface calculations, where the ICD's are essential in describing the shape of the charge density at the surface, a similar phenomenon has been experienced.¹⁴

However, by using the bare Fourier coefficients in the vector, all elements of the vector converged. In effect, this choice of the elements put the vector in the correct part of the solution space—a judicious choice of the vector. Note, one cannot exclude these coefficients from the vector since they describe the interstitial charge density and make the vector charge conserving. So, the physics of the particular problem should be a guide to the choice of the elements in the vector, as well as a guide to placing the vector in the correct region of solution space.

Seventh, in instances where simple mixing works very well, there will probably be no increase in convergence. This is a reflection of the complexity of the problem. If the solution space of the problem is rather linear, then using a nonlinear mixing will not be highly beneficial. This has been experienced when the method was applied to Slater-Koster, tight-binding coherent-potential calculations.¹⁵ In paramagnetic alloy calculations, where simple mixing worked well, the new method did not improve the convergence, although it did not worsen it. However, when the same calculations were applied to complex lattices with *f*-electron atoms, the convergence was improved by at least a factor of 2.

Finally, the particular example and method used to showcase this version of Broyden's technique is but one type of electronic-structure calculation. The molecular-dynamics (MD) electronic-structure approach, introduced by Car and Parrinello,¹⁶ for the study of the dynamical properties of low-symmetry, multiatom systems may also employ the present convergence method. For example, Pederson¹⁷ has applied the above method by mixing the electronic potentials to improve the rate of convergence in MD-based calculations which use a Gaussian-orbital technique. The convergence was improved by a factor of 2. Since there are a number of input-output vectors that occur in the MD-type algorithms, another possible application comes to mind; that is, employ the present method to mix the wave-function coefficients (such as the plane-wave coefficients or the Gaussian-orbital parameters) instead of, or, perhaps, in conjunction with, the mixing of the electron density or potential. So, we emphasize that the improvement of convergence in iterative calculations is of general interest and the present mixing scheme may be applied to a variety of computational physics problems with benefit.

V. RESULTS

Two separate tests were made of this algorithm. In the first, the above method and Srivastava's method were

compared using the simple test case given in the paper of Vanderbilt and Louie. We found similar results, as we should since the comparisons are equivalent. The present method always converged more rapidly than Srivastava's method for all linear mixing parameters α and weights tested. Also, it was noted that G converged to the correct value in the present method, whereas in the standard Broyden's method this was not the case. This should be the case since G was required to satisfy Eq. (8) for all previous iterations, as does the true inverse Jacobian.

In the more substantial second test, we performed Korringa-Kohn-Rostoker (KKR)-CPA coherent-potential-approximation¹⁸ calculations of the random, binary, ferromagnetic alloy $\text{Ni}_{0.35}\text{Fe}_{0.65}$, which is on the verge of magnetic collapse. For lattice constants near the experimental value, $a = 6.60$ a.u., it is magnetic. However, while minimizing total energies with respect to lattice constant, it is found that a 5% reduction in volume results in a collapse of the local ferromagnetic moments.

As mentioned in the Introduction, this sort of instability can cause divergence, or allow convergence, for many mixing algorithms. Below we give a comparison of the present method to both simple mixing and Anderson mixing, which has been an extremely good algorithm for convergence in many previous cases.

In Fig. 1, we demonstrate how the charge density converges as a function of iteration. The ordinate is actually the negative inverse of the natural logarithm of the rms of the total charge density. For the case of perfect convergence, this quantity should go to exactly zero. Of course, in practice what we accept as converged happens much earlier than this. From the figure, we see that the current method approaches zero more rapidly than Anderson's method. Evidently, both methods are superi-

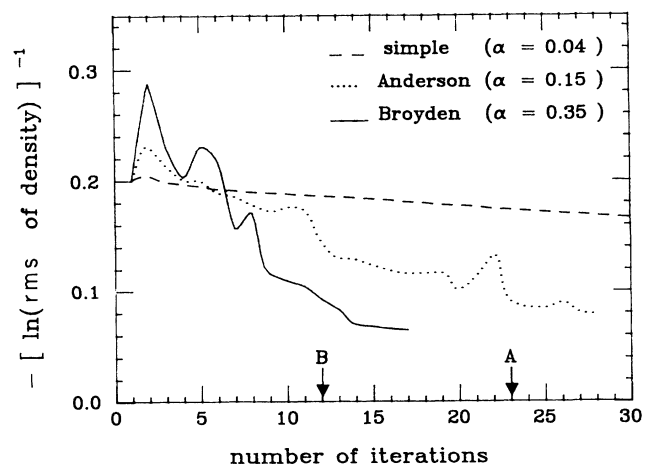


FIG. 1. A comparison of the convergence of the charge density vs iteration number for simple mixing, Anderson's method, and the modified Broyden's method is presented. The ordinate approaches zero as convergence proceeds. The arrow A (B) marks where the total energy is converged for the Anderson (modified Broyden) method. See the text for a description of what defines convergence.

or to simple mixing in this respect.

In order to be as fair as possible in the comparison, it was attempted to optimize α in the simple mix and the Anderson methods. α was 0.04 and 0.15 for the simple mix and Anderson methods, respectively. For α greater than these, the calculations would diverge. In the modified Broyden's method, α was chosen arbitrarily to be 0.35. This value of α was rather large compared to those values used in the other methods; as a consequence of this, it did not satisfy Powell's criterion and resulted in divergence for the first two iterations, where the vector is just simple mixed. The weight w_0 was chosen to be 0.01.

It should be noted in these calculations that the modified Broyden's procedure was carried out initially for seven iterations in which only the charge density was in the vector and the magnetization density was simple mixed with a mixing parameter of 1.5. This had three effects: (1) the magnetization density was rapidly reduced, (2) the associated large charge oscillations were damped by the modified Broyden's procedure, and (3) no memory effect was left in since we stopped after seven iterations and discarded the iteration history.

In iterations thereafter, if the charge and magnetization densities were continued to be mixed in that way, the energy and pressure would converge to the correct values in about the same number of iterations, but with a rms difference of the charge density no better than the Anderson method. Although the modified Broyden's is a more stable method, a higher rms difference resulted because of the fluctuations in the size of the moments, about $(10^{-2} - 10^{-3})\mu_B$, due to the simple mixing of the magnetization. However, after seven iterations, if the Broyden vector was composed of both the total charge and magnetization densities of the Ni and Fe sites, a drastic drop in the rms difference results, since the size of the moment fluctuations is stabilized to $10^{-6}\mu_B$ very quickly. (There was no special reason to restart the calculation after seven iterations, but that was enough to stabilize the charge and magnetization fluctuation.)

Note that in Fig. 1 the large fluctuation in the fifth iteration is due to a large drop in the local moments towards zero, which in turn creates a "large" charge oscillation. Note, however, that within two iterations the modified Broyden's method has damped out the oscillation. The fluctuation in the rms in the eighth iteration is due to the simple mix which occurs when Broyden's method is restarted, since Powell's criterion was not used in the choice of α . Note, this fluctuation is not as dramatic as in the first few iterations because the calculation is closer to convergence.

For the simple mixing and the Anderson method during the first seven iterations, the magnetization was simple mixed with a mixing of 1.5, as was done in the Broyden method, to allow the moments to rapidly reduce their magnitude; thereafter the magnetization's mixing was 0.95. Since neither method is a multi-r-point update, it takes longer for the charge density and magnetization density fluctuations to die down; this is evident from Fig. 1.

The stability of the methods is more indicative of their value. In Fig. 2., we plot the deviation of the pressure

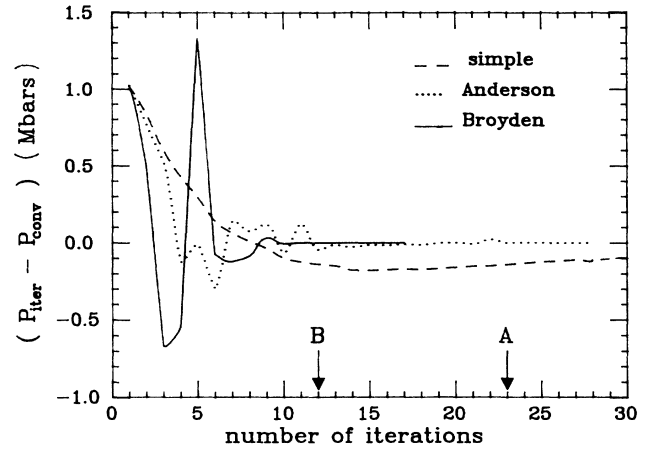


FIG. 2. Convergence of the pressure relative to the converged pressure iteration number is shown for the three methods. A (B) refers to the same thing as in Fig. 1. Relative errors in the pressures are less than ± 0.01 kbar.

from the converged pressure versus iteration number. The calculation was considered converged when the pressure was in error by less than ± 0.01 kbars. The pressure is a sensitive indicator of the efficacy of each method since it converges linearly in the charge density of fluctuations, unlike the total energy which converges quadratically in the fluctuations.¹⁹ Except for the large fluctuations in the pressure associated with the large choice of α in the initial two iterations and with the damping of the charge oscillation at the fifth iteration, the modified Broyden's method is an extremely stable method due to its multi-r-point updating. By following Powell's criterion for the choice of α more strictly, the convergence might have been faster, or at least the initial fluctuations would have been less dramatic.

VI. CONCLUSION

A modified version of Broyden's quasi-Newton-Raphson method was presented which incorporates the best qualities of two methods proposed previously by Srivastava and by Vanderbilt and Louie. It was found to always converge in fewer iterations than Srivastava's method, which was due to the fact that the inverse Jacobian converges much more rapidly to its true value in the modified version. This method requires less computer storage and fewer multiplications than the VL method because only m vectors of length N need be kept, yet has the added flexibility of the weighting factors for each iteration. Implementation of the method is no more difficult than Srivastava's method, and, in reality, no more difficult than Anderson's method which includes three or four charge densities.

The stability of the method is its most important aspect. Noise levels in the calculations are reduced in some instances by orders of magnitude. This results in rapid convergence with extremely stable values. For extremely sensitive electronic-structure calculations, such as, on surfaces, Broyden's algorithm can obtain convergence

where other methods fail. With the large amounts of central-processing-unit time required for many electronic-structure calculations, the associated benefit is a large savings of computational resources.

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APPENDIX

Equation (12), the general form of the inverse of Eq. (11b), is derived. There is a more rigorous derivation, however, the following derivation is most straightforward.

From Eq. (11b),

$$B^{(m+1)} = w_0^{-2} \left[I + \sum_{n=1}^m |\Delta \bar{F}^{(n)}\rangle \langle \Delta \bar{F}^{(n)}| \right], \quad (\text{A1})$$

where $|\bar{\Delta F}^{(n)}\rangle \equiv (w_n/w_0)|\Delta F^{(n)}\rangle$. If the second term in Eq. (A1) gives small corrections to each element of the unit matrix, then the infinite expansion of $(B^{(m+1)})^{-1}$ is defined. Then, using implied summation, we have

$$(B^{(m+1)})^{-1} = w_0^{-2} [I + |\Delta \bar{F}^{(n)}\rangle \langle \Delta \bar{F}^{(k)}| \times (\delta_{nk} - \bar{a}_{kn} + \bar{a}_{ki}\bar{a}_{in} - \dots)], \quad (\text{A2})$$

where we define $\bar{a}_{ij} = \langle \Delta \bar{F}^{(j)} | \Delta \bar{F}^{(i)} \rangle$.

By now resumming the infinite series in Eq. (A2), and using the usual summation convention, we obtain

$$(B^{(m+1)})^{-1} = w_0^{-2} \left[I + \sum_{n,k=1}^m w_n w_k |\Delta F^{(n)}\rangle \langle \Delta F^{(k)}| \times (w_0^2 I + a)^{-1}_{nk} \right], \quad (\text{A3})$$

where $a_{ij} = w_i w_j \langle \Delta F^{(j)} | \Delta F^{(i)} \rangle$. Equation (A3) is the same as Eq. (12) given in the text and the definition of β_{nk} is obvious.

This can be considered a generalization of Householder's modification formula.²⁰

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⁶Essentially, the majority and minority charge densities undergo long-wavelength fluctuations of comparable magnitude through Poisson's equation. This leads to constructive (destructive) interference in the sum (difference) of the two. Thus, the magnetization, which is the difference of the two, is less affected locally. Another way to see this is to note that within the local-density approximation the magnetization density at a given point in space is dependent on a local exchange-correlation functional, which is less affected by long-wavelength changes in the density.

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¹¹For a nonmagnetic, binary, disordered alloy ($A_c B_{1-c}$) calculation using the KKR-CPA, there are two charge densities in the vector $|n^{(m)}\rangle = |n^A(r_1), \dots, n^A(r_n), n^B(r_{n+1}), \dots, n^B(r_{2n})\rangle$. Defining a vector transpose $\langle f(r_i) | \equiv \langle c_1, \dots, c_n, (1-c)_{n+1}, \dots, (1-c)_{2n} |$, charge neutrality is established if $cZ_A + (1-c)Z_B = \langle f(r_i) | n^{(m+1)}(r_i) \rangle$, where c [(1-c)] and $Z_{A[B]}$ are the concentration and the atomic numbers of the A

[B] atoms, respectively. As long as $\langle f |$ is independent of iteration and the initial guess of the charge densities is charge conserving, it is easily shown that all of Broyden's methods are charge conserving. For a given definition of the vector n , an appropriate definition of the vector f can be chosen.

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