Theory of non-linear electron-phonon coupling and its first-principles implementation

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Significant efforts have been dedicated to developing first-principles methods that accurately model the influence that
quantum and anharmonic effects on the nuclei dynamics have on the structural, vibrational, and superconducting properties of materials. However, the electron-phonon interaction is conventionally treated using a linear approximation, which involves truncating the expansion of the electron-nuclei potential with respect to the displacements of the nuclei after the first term. This approach may be inadequate in cases where quantum and anharmonic effects are pronounced, such as in superconducting hydrides or systems undergoing charge-density wave or ferroelectric transitions. To address this limitation, a new non-perturbative framework for electron-phonon coupling is proposed, which can be implemented from first principles. When applied to superconducting palladium hydrides, higher-order non-linear contributions are found to be surprisingly comparable in magnitude to the standard linear term. These non-linear effects are crucial for accurately explaining the superconductivity and the inverse isotope effect observed in this system. More generally, the proposed approach could significantly impact ab initio calculations of electron-phonon interaction-related properties, including superconductivity and electrical conductivity, in materials where quantum and anharmonic effects on the nuclei dynamics play a crucial role.